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Classification of the Spectral Lines of Cl, Br and I

By

Kwan-ichi Asagoe

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Abstract

The spectral lines of chlorine, bromine and iodine were first classified into arc and spark types by observing, (1) the effect of constriction of a part of a Geissler tube upon the intensities of the lines, (2) the change of relative intensities called forth by putting a capacity in the circuit, and (3) the effect of insertion of a self-induction in the condensed heavy discharge circuit.

Then the spark lines were further sorted out into spark, supper-spark lines etc. by investigating the exciting stages. The various excitation conditions were obtained by (1) varying the intensity of a magnetic field applied to the Geissler tube and (2) capacity and (3) self-induction placed in the circuit.

Thus all the spectral lines of these elements lying in the region covering visible and ultra-violet (up to 2000 A) were classified. Arc lines are found only in the visible region, while spark lines are distributed all over the entire region investigated. Super- and super-super-spark lines lie generally in the more refrangible side.

In order to find certain series relations which may exist among lines of the spectra of halogen elements, chlorine, bromine and iodine, classification of the lines into arc and spark types, and further of spark lines into spark, super-spark, etc. is the first problem to be studied. The present investigation was undertaken for this purpose.

I Classification of the Spectral Lines of the Halogen Elements into Arc and Spark Types

The following three methods were employed to determine the types of lines.

(1) *The first method* was the same as that used by Kimura. He studied the lines of iodine[1] and bromine[2] with a small glass prism

1 These Memoirs, **4**, 167 (1920)

2 These Memoirs, **4**, 127 (1920)

spectroscope. In the present experiment, these were re-examined minutely with a spectrograph having a higher dispersion, and the examination of the chlorine spectrum was extended to the region lying from the red to the ultra-violet.

A piece of an ordinary glass tube of about 5 mm. diameter, (in the ultra-violet region, a quartz tube of 3 mm. diameter was used), was drawn into a conical capillary, the narrowest part being about 0.2 mm. in diameter and 5 mm. in length. The constricted capillary thus obtained was used in place of an ordinary one as a part of a discharge tube (say, Tube I). The tube was simply excited by a 20 cm. induction coil. A well defined vertical image of the glow in this conical part was formed on the spectrograph slit, and the light coming from various parts of the cone were simultaneously photographed on a plate.

It was observed that certain lines strongly emitted from the wide part disappeared from, or weakened in intensity in the capillary, while a number of faint lines presented in the former were remarkably enhanced in the latter. Thus lines in the spectrum may be divided into the two types according to the mode of their appearance.

Now, the current density and the potential gradient in the wide part of the tube would both have smaller values than those in the constricted portion. Hence it is evident that much energy will be required to excite lines of the latter type. It is then natural to regard the lines of the first type as arc lines, and those of the second as spark ones.

In order to test the correctness of this consideration, lines of the spectra of tin and antimony were first examined by this method. A small quantity of $SnCl_4$ (or $SbCl_5$) was poured into a small glass cup, and this was connected to the discharge tube by a very fine capillary drawn from a piece of glass, the length of which was about 50 cm. The spectrum of the light emitted from the conical part of the tube was then photographed, the pump being operated during the exposure to the spectrograph. In this case, however, a condensed discharge was sent through the tube. Since the vapour of $SnCl_4$ (or $SbCl_5$) was flowing through this constricted portion, the lines of tin (or antimony) were excited in company with chlorine lines. The spectrum of $SnCl_4$ thus taken is reproduced in Pl. I, Fig. 1. Fig. 2 represents the spectrum of a spark produced between electrodes of tin. Comparing these two, we see that in Fig. 1, the spark lines and super-spark

lines of tin[1] were easily sorted out, lines marked with one dot denoting the spark lines, and those with two dots the super-spark ones of tin. Thus the results obtained by the two different methods are in harmony with each other, and this shows that the method mentioned above is suitable for classifying the lines of gaseous elements into the arc and spark types.

(2) *The second method* is to investigate the change called forth in the relative intensities of lines when a capacity is inserted in a circuit parallel to a discharge tube. An ordinary Geissler tube having a main tube of about 3 mm. diameter and about 25 cm. length (say, Tube II) was simply excited by the 20 cm. induction coil, and the light thus emitted was examined. We see that the spectral lines already classified as arc lines in the first method were stronger, while spark lines were fainter or entirely unexcited. On the other hand, by the insertion of a condenser of a capacity of about 0.003 μF in the circuit, the arc lines were suppressed, while the spark lines were enhanced. The two spectra were taken one above the other on a photographic plate as seen in Fig. 4, the same exposure being given to each spectrum. The relative intensities of the lines in these two spectra being examined, the lines were easily classified into arc and spark ones. The result thus obtained coincided with that of the first method.

(3) *The third method.* Changes called forth in the spark spectra of the halogen elements by putting a self-induction in the discharge circuit were next investigated. Carbon electrodes were placed in a tube of fused silica filled with the vapour or the gas of the elements and sparks were passed through the electrodes by the discharge from a condenser charged up by a Thordarson transformer of 3/4 kVA, giving 10,000 volts in the secondary, and the spectrum was taken. Next, an appropriate self-induction was put in the discharge circuit, and then the second spectrogram was taken. Comparing these two (see, Fig. 5, in Pl. I), we see that, in the latter spectrum, lines classified as spark type in the above two experiments were weakened, while those of the arc type were rather enhanced.

The three methods mentioned above gave results concordant with each other, and thus we can determine decidedly the types of lines, arc or spark, except in the case of a few very faint lines. The result of the experiments will be given below.

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1 Japanese Journ. Phys., **3**, 197 (1924)

The visible region of the spectrum to be studied is divided into three parts, namely λλ 6600-4500, 4600-4100 and 4200-3500. In the first two regions, a three glass prism spectrograph, having an achromatic camera lens of 50 cm. focus, was used, the linear dispersion on the photographic plate being about 0 02 mm. per 1 A at H_α and 0.076 mm. at 4600 A in the first setting, and 0 082 mm. at 4520 A and 0.137 mm. at 4170 A in the second. In the remaining region, two prisms were employed, which gave a dispersion of 0.060 mm. at 4100 A and 0.144 mm. at 3540 A. The ultra-violet region was photographed with a small Hilger quartz spectrograph (E31). Rapid process panchromatic plates were employed for all the regions.

Results

(I) Iodine

Goldstein[1] and Nutting[2] have observed a change called forth in the iodine spectrum by putting a capacity in the discharge circuit. But their results were only fragmental. The spectrum was then studied minutely by Wood and Kimura[3], and the many lines lying in the region between 6585 A and 4632 A were sorted out into arc and spark types. Kimura[4] has also investigated the spectrum by the first method described above. The arc lines lying in the Schumann region were investigated by Turner[5]. Quite recently, L. and E. Bloch[6] have studied the spark lines of iodine, and also selected out several arc lines in the visible region. In the present experiment, the region extending from the visible to the ultra-violet (up to about 2000 A) was examined minutely, and the result obtained was compared with those of the previous investigators.

A small quantity of well-dried potassium iodide was put in a glass cup having a platinum wire sealed in at one end and this was again sealed in an outer tube. Two tubes of such construction were connected to a discharge tube and these were used as the electrodes. During the evacuation, the glass walls of the tube were strongly heated by a Bunsen flame and a heavy discharge was sent through. The

1 Astrophys. J., **27**, 25 (1908)
2 Astrophys. J., **19**, 239 (1904)
3 Astrophys. J., **46**, 181 (1917)
4 Loc. cit.
5 Phys. Rev., **27**, 397 (1926)
6 Ann. de Physique, **11**, 141 (1929)

tube was then sealed off from the pump, when the discharge gave a bright green glow.

When a tube having a constricted capillary of about 0.2 mm. diameter was excited simply by an induction coil, a glow of yellowish orange colour appeared in the wide part, and a bluish green one in its capillary. The spectrum of the latter consisted of iodine lines, while that of the former consisted of lines, fluted bands and continuous bands. A similar change in the spectrum of the glow in Tube II was also noticed, a weak excitation giving the yellowish orange spectrum, while the condensed discharge gave the bluish green one.

Strong lines in the spectrum of the yellowish orange glow, were λλ 5119, 4917, 4897, 4862 and 2062, and these were reduced in intensity or entirely disappeared in the green spectrum, and consequently these may be considered as arc lines. Most of these arc lines lie in the region beyond 4100 A, none being found in the more refrangible region between 4100 A and 2062 A. In the Schumann region, a number of arc lines were observed by Turner, and we could also photograph the lines at λλ 1876, 1845 and 1830 in addition to the line at 2062 A, when a photographic plate was bathed in paraffin oil and over-exposed. On the other hand, spark lines which were strongly enhanced in the green spectrum, were found in the whole region of the spectrum investigated, the strongest lines being

λλ 5613, 5497, 5465, 5407, 5405, 5161, 4676, 4667, 4453, 4445, 4424, 4410, 4236, 3940, 3931, 3498, 3482, 3303, 3288, 3275, 3194, 3055, 2994, 2879, 2809, 2730, 2675, 2566, 2465, etc.

Now, a pair of carbon electrodes was placed in a silica tube of about 2 cm. diameter having a side tube containing a certain quantity of iodine crystals. The side tube being heated by a Bunsen burner, the tube was filled up with a dense vapour of iodine, and after this condition was reached a spark was started between the electrodes.

In the spectrum of the heavy condensed discharge, the spark lines of iodine were strongly developed, some of them being broadened on both sides, and the others unsymmetrically on the red side; and no arc lines were found. However, when a considerably large self-induction was put in its circuit, the strongest lines of the arc type, i. e, λλ 5119, 4917 and 4862, were developed as faint lines showing diffuse wings on the red side.

The lines of iodine were thus classified into arc and spark types, and the results obtained are shown in Table I with the relative intensities of the lines. The wave-lengths of the lines from the red to 4632 A were taken from the measurements made by Wood and Kimura[1], and those of the lines lying between 4632 A and 3030 A from the table given by Konen[2]. The lines shorter than 3030 A, and some arc lines lying in the blue and violet region (these lines are marked with asterisks) were newly determined by the present writer from the spectrogram of a Geissler tube with an iron comparison photographed with a Hilger quartz spectrograph (size E1), international wave-length unit being used. In the sixth column, the results of the previous investigators are shown. The coincidence of these results is perfect except in the case of a few faint lines.

(II) Bromine

Goldstein[3] and Nutting[4] have already noticed the multiplicity of the bromine spectrum. Kimura[5] examined the spectrum of this element minutely and classified the strong lines of the spectrum into arc and spark types, using a method similar to the first one described above. The arc lines lying in the Schumann region were observed by Turner[6]. Recently L. and E. Bloch[7] have also sorted out some arc lines in their study of the spark lines of bromine.

The tubes employed in the present investigation were prepared similarly to the iodine ones, potassium bromide being used as electrodes. When the discharge was sent through the tube, the wide part of Tube I was filled up with a glow of chamois yellow, while a blue light was emitted from the capillary portion; in Tube II, the colour of the light also varied in a similar manner when a capacity was placed in the circuit.

The light emitted from the capillary portion consisted of the line spectrum of bromine and that from the wide part, of lines, fluted bands and continuous bands. We see that the strong lines in the red region,

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1 Loc. cit.
2 Kayser's Handbuch der Spektroskopie, **5**, p. 574
3 Loc. cit.
4 Loc. cit.
5 Loc. cit.
6 Loc. cit.
7 Ann. de Physique, **7**, 207 (1925)

i. e., λλ 6632, 6560, 6351, 6150 and the bright lines in the blue, i. e., λλ 4781, 4752, 4615, 4576, 4526, 4478, 4473 and 4442 are characteristic lines of the chamois yellow spectrum, but their intensities are much reduced in the blue spectrum. Besides these, there are, however, many lines enhanced in the blue spectrum. Among these, the lines at

λλ 5332, 5238, 5194, 5184, 4931, 4929, 4817, 4786, 4743, 4720, 4705, 4679, 4366, 4224, 4180, 3987, 3981, 3562, 3418, 3350, 3333, 3074, 2972, 2969, 2927, 2594, 2557, 2541, 2522, 2395, 2392, 2390, 2389, 2387, etc.

are the strongest. Thus we consider the former group of lines as arc lines, and the latter as spark ones. We see that the spark lines are distributed all over the entire region investigated, while the lines of the arc type are found only in the visible region beyond about 3700 A, and can not be detected in the ultra-violet. But in the Schumann region, as reported by Turner, many arc lines seem to be emitted.

In the spectrum of a spark discharge between carbon electrodes placed in a dense vapour of bromine, the spark lines were strongly developed, some of them being broadened out on both sides, others unsymmetrically on the red side, while the arc lines were seen faintly showing diffuse wings on the red side. By the insertion of a self-induction in the discharge circuit, the spark lines mentioned above were suppressed strongly, while the lines of the arc type were enhanced.

Table II records the result thus obtained, the wave-lengths of the lines from the red to 3699 A being taken from the tables[1] given by Eder and Valenta and Galitzin and Willip; while those shorter than this, and also a number of arc lines in the visible region (they are marked with asterisks in Table II) were newly measured by the present writer. Kimura's result is given in the sixth column; these two results are in harmony.

(III) Chlorine

Lines of chlorine at λλ 4661, 4601, 4526 and 4390 were noticed by Goldstein[2] to show an arc character. Nutting[3] has also observed the multiplicity of the chlorine spectrum. Nelthorpe[4] has found about twenty lines of chlorine which disappeared from the "Grundspektrum",

1 Kayser's Handbuch der Spektroskopie, **5**, p. 182
2 Loc. cit.
3 Loc. cit.
4 Astrophys. J., **41**, 16 (1915)

and he regarded these lines as of arc type. Turner[1] has investigated the spectrum in the Schumann region, and found several arc lines. Most recently, several lines lying in the visible region were selected out as of an arc type by L. and E. Bloch[2].

Electrodes provided with pure, well-dried sodium chloride were used in the present work. When the tube was sealed off from the pump, the carbon monoxide bands soon appeared and also the gas pressure increased gradually, so that to get rid of these troubles the tube was connected to the pump during the exposure to the spectrograph.

The tubes first used in this experiment had nearly the same dimensions as those employed in the case of iodine and bromine. The results, however, were found to be unsatisfactory. Then a fine capillary of about 0.1 mm. diameter was drawn from a piece of a narrow capillary tube having a diameter of 1 mm, and by using this as a part of Tube I, a fairly good result was obtained when a small spark gap was put in the discharge circuit. In the second method, a condenser of a slightly larger capacity was necessary in order to weaken the arc lines.

The wide part of Tube I was filled up with a glow of bluish gray, while a green light was emitted from the capillary portion. A similar change in the glow was noticed in Tube II when a capacity was placed parallel to the tube.

The green spectrum chiefly consisted of lines of chlorine, while the bluish gray one consisted of lines, fluted bands and continuous bands. Enlarged reproductions of the spectra obtained from Tubes I and II are given in Figs. 3 and 4 respectively.

Lines whose intensities were suppressed in the capillary part or under the heavy excitation chiefly lie in the region from 4700 A to 4200 A, stronger lines of which are

$\lambda\lambda$ 4661, 4601, 4526, 4491, 4439, 4404, 4390, 4380, 4370, 4324, etc.

These are regarded as arc lines. Lines of spark type behaving just opposite to the former, however, are distributed all over the whole region of the spectrum examined, the following being the strong lines :—

$\lambda\lambda$ 5457, 5444, 5423, 4820, 4810, 4795, 4373, 4344, 4309, 4254, 4241, 4234, 4133, 3861, 3851, 3846, etc.

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1 Loc. cit.

2 Ann. de Physique, **8**, 397 (1927)

Nearly all the lines of chlorine could be excited in a spark produced between carbon electrodes placed in a silica tube through which chlorine gas was flowing. Of the spark lines, some show broad wings on the red side and others symmetrical ones, while the arc lines have diffuse wings on the red side. Again, as will easily be seen in Fig. 5, the insertion of a self-induction in the circuit markedly reduced the intensities of the spark lines mentioned above, while the arc lines classified above developed rather strongly.

The result thus obtained is recorded in Table III, the wave-lengths of the chlorine lines longer than 3353 A being taken from the table given by Eder and Valenta[1], and those for shorter ones from the Jevons[2] measurement. Lines selected out by Nelthorpe as of an arc type are shown in the sixth column ; coincidence of the two results is satisfactory except in the case of three lines at $\lambda\lambda$ 3982, 3872 and 3854. De Bruin[3] has remarked some regularities in the arc spectrum of chlorine. It seems to the present writer, however, that most of the lines studied by him are not of the arc type.

Recently, Dr. Laporte[4], during his stay in Kyoto, found that the arc lines in the visible region sorted out by the present writer form the combination $4s^{4,2}P$-$4p^{4,2}(S,P,D)$, the frequency differences between the five lower levels being 530.4, 338.7, 1399.1 and 640 8 cm^{-1}.

II Further Classification of the Lines of Spark Type into Spark, Super-Spark Lines, etc.

It is known that if a magnetic field is applied to a discharge tube the discharge path is affected and the glow is strengthened on one side of the tube, resulting in the increase of the current density. Thus, by adjusting the intensity of the magnetic field, we can regulate the current density in the path of the discharge or the intensity of excitation. If spectra of the Geissler tube are taken under increasing magnetic fields, arc, spark, super-spark, etc. lines will probably appear in succession, and by this means also the lines may be sorted out into arc, spark, super-spark etc.

In order to ascertain the correctness of this consideration, the spectrum of $SbCl_5$ was first examined. The short capillary part (diam.

1 Kayser's Handbuch der Spektroskopie, **5**, p. 307
2 Proc. Roy. Soc., **103**, 193 (1923)
3 ZS. f. Phys., **39**, 869 (1926)
4 Nature, June 30, p. 1021 (1928)

= 1.9 mm.) of a Geissler tube was horizontally mounted between truncated pole pieces of an electro-magnet of the Du-Bois type. As already mentioned above, a small glass cup filled with $SbCl_5$ was connected to the tube by a very fine capillary of glass. The pump being operated during the exposure, the tube was excited by a 20 cm. induction coil, and the image of an end-on emission from the capillary part was projected on the slit of a spectrograph. In this experiment, a Hilger wave-length spectrograph and a Fuess quartz spectrograph (model B) were used.

The intensity of the magnetic field was varied gradually, from zero to 350, 1270, 2300, 3750 and 5570 gausses successively. The spectra of $SbCl_5$ emitted under these magnetic fields were taken one above the other on a photographic plate, an exposure of 75 minutes being given to each spectrum. Enlargements of the spectrograms thus obtained are reproduced in Pl. II, Fig. 7. Fig. 6 represents the spark spectrum of antimony, spark, super-spark and super-super-spark lines being marked with one, two and three dots respectively according to the result of Kimura and Nakamura[1].

Now, as is easily seen from Fig. 7, spark lines of antimony, for example, $\lambda\lambda$ 3241, 3041, 2981 and 2966, are developed in all the spectra with nearly equal intensities. Super-spark lines at $\lambda\lambda$ 2913, 2791, 2671 and 2617 are very faint or not developed in the spectrum taken under the lowest field, but strongly increased in intensity as the field intensity was strengthened. Super-super-spark lines, $\lambda\lambda$ 2857, 2741 and 2632, however, are seen only in the spectrum taken under the highest magnetic field. Thus we can easily sort out the lines into spark, super-spark and super-super-spark by this method, and the result thus obtained coincides perfectly with that of Kimura and Nakamura. This shows that by this method also the lines of gaseous elements can be classified into arc, spark, super-spark ones etc.

Using the same tube mentioned above, we then proceeded to see the influence of the variation of the capacity and self-induction in a discharge circuit upon the spectrum. The capacity or the self-induction were varied step by step, and the corresponding spectra were taken. Figs. 8 and 9 in Pl. II represent the spectra thus obtained by changing the capacity and self-induction respectively, exposure times, as shown in Figs., being so regulated that certain lines behaving similarly

1 Loc. cit.

would be impressed with nearly equal blackness in all the spectra. By examining the behaviours of the lines in these spectra, the lines were easily classified into three classes and they corresponded exactly to the spark, super-spark and super-super-spark lines of antimony determined already by the first method.

Thus the three methods mentioned above were ascertained to give the same result, and we then proceeded to investigate the spectra of iodine, bromine and chlorine employing these methods. The results so far obtained will be described below.

Results

(I) Iodine

The tube used was of the form similar to the $SbCl_5$ tube (diameter of the capillary was 1.1 mm.), but with electrodes of potassium iodide. During the evacuation of the tube, heavy discharges were sent through and the walls of the tube were highly heated. After such treatment, the tube was sealed off from the pump when the iodine vapour got a suitable pressure. When the intensity of the magnetic field was increased gradually, the colour of the glow changed from yellowish orange to bluish green. The same phenomenon was also observed in the experiments in which the capacity and the self-induction were varied. The photograms obtained are reproduced in Pl. III. Figs. 10, 11 and 12 represent the spectra taken varying the imtensity of the magnetic field, the capacity and the self-induction respectively, exposure times being also given in the figures.

Iodine lines were sorted out into four classes. The intensities of lines of the first class were suppressed when the field intensity or capacity was increased, and also when the self-induction was reduced. These lines correspond to the arc lines (I I) classified already. Lines belonging to the second class, as will be seen in the reproduction, at $\lambda\lambda$ 2730, 2689, 2675, 2611, 2583, 2566, 2461 and 2408, have nearly equal intensities in all the spectra. Lines of the third class, for example, $\lambda\lambda$ 2949, 2873, 2837, 2759, 2705 and 2344, are very faint or missing in the lowest spectrum, but their intensities increase gradually in the upper spectra as can easily be seen in the photograph. Typical lines of the fourth class are $\lambda\lambda$ 3005, 2918, 2547, 2520 and 2426. They are not developed in the lower spectra, but they appear in the third or the fourth one, their intensities increasing so rapidly that lines of this class can be easily differentiated from those of the third class.

The lines belonging to these classes are regarded as the spark (I II), super-spark (I III) and super-super-spark (I IV) spectrum of iodine respectively. The results thus obtained are recorded in the fifth column of Table I.

While the present experiment was going on, L. and E. Bloch[1], employing a method of an electrodeless discharge, sorted out the spark lines into I II, I III and I IV. Coincidence of my result with Bloch's is perfect with respect to the spark lines. But their selection of arc lines seems to be unsatisfactory.

(II) Bromine

Tubes similar to that used in the study of iodine were employed, potassium bromide being used as the electrodes. The experiment being conducted quite similarly to the case of iodine, BrI, BrII, BrIII and BrIV (unfortunately the wave-lengths of lines of this class were not measured) were easily selected out. The result is recorded in the fifth column of Table II, and compared with that obtained by L. and E. Bloch[2]. These two results are in harmony with respect to the spark lines.

(III) Chlorine

Similar tubes to the above (capillary diameter about 0.7 mm.) were employed, sodium chloride being used as the electrodes. The pump was operated while the spectrograms were being taken.

Intensity of Magnetic Field	Exposure Time
8,000 gausses	55 minutes
3,950 „	62 „
2,300 „	75 „
680 „	92 „
0 „	105 „

In a preliminary experiment, the same exposure was given to each spectrum taken under different magnetic fields, but the results were unsatisfactory until the exposure times were so regulated that similarly behaving lines would be impressed on a photographic plate with nearly equal intensities in every spectrum. The exposure times thus adjusted are shown in the foregoing table, with the corresponding field intensities.

1 Ann. de Physique, **11**, 141 (1929)
2 Ann. de Physique, **7**, 207 (1925), and **9**, 554 (1928)

Chlorine lines were sorted out as arc, spark and super-spark lines, no super-super-spark line of chlorine being found; such lines would perhaps not be emitted under the excitation used in the present experiment. It may be worthy of mention that a greater amount of energy seems to be required to excite spark lines of chlorine, especially of Cl III and Cl IV, than those of iodine and bromine.

The result obtained is shown in the fifth column of Table III. Comparing this with the results of Paschen[1] and L. and E. Bloch[2], coincidence of these three is perfect in regard to the spark lines.

Summary of the Results

Besides the lines listed above as arc type, there may be combination lines whose emission is forbidden by the selection principle. Such lines may, in general, be emitted in a strong electric or magnetic field, and hence they may also behave in a manner similar to spark lines. It seems, however, to be difficult to distinguish these lines from the spark ones by our methods. Therefore, such lines, if excited, may have been included in spark lines in Tables I, II and III.

Examining the results obtained minutely, the following facts seem to be established.

(1) These halogen elements, chlorine, bromine and iodine, have a number of arc lines in the visible region; no arc line could be found in the ultra-violet region examined except intense lines of iodine at $\lambda\lambda$ 2062, 1876, 1845 and 1830.

(2) On the contrary, spark lines emitted by singly ionized atoms of these elements are distributed all over the entire region investigated.

(3) Super-spark lines due to doubly ionized atoms are found chiefly in the ultra-violet region, super-super-spark lines lying generally in the more refrangible side.

(4) The modes of broadening of the lines of these elements observed already by the present author[3] are shown in the seventh column of Tables I, II and III, in which 1), 2) and 3) denote the first, second and third type of the broadening respectively. As can easily be seen in the tables, lines of the first type all belong to the arc spectrum, while those of the second and third types belong to the spark one. Nearly all lines of the third type, which suffered large shifts when

1 Ann. d. Phys., **71**, 559 (1923)
2 Ann. de Physique, **8**, 397 (1927), and **11**, 554 (1928)
3 These Memoirs, **10**, 15 (1925), and Japanese Journ. Phys., **4**, 85 (1927)

the pressure of the gas and the current density were increased, belong to the spark spectrum of the first order. The remaining few of this type are the super-spark or super-super-spark lines, but the displacements of such lines are, in general, comparatively small.

In conclusion, the writer wishes to express his hearty thanks to Prof. M. Kimura, under whose direction this work was done.

Table I, Iodine

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
6585.0	3 : 5		2 : 5		—		S II	. 9)
83.2	2 : 0		2 : 0		—		A I	5) 8)
38.3	0 : 2		0 : f		—		S III	5)10)
16.1	1 : 3		0 : 3		—		S II	2) 9)
6488.1	2 : 1		1 : 0		—		A I	5) 9)
76.0	0 : 1		—		—		S III	. 10)
40.2	0 : 1		0 : f		—		S III	. 10)
6359.1	2 : 1		1 : 0		—		A I	5) 8?)
39.5	4 : 2		4 : 2		—		A I	2) 5) 8?)
20.9	0 : 1		0 : 1		—		S III	. 10)
13.1	1 : 0		f : 0		—		A I	5)
6296.4	2 : 0		1 : 0		—		A I	5)
93.9	3 : 0		2 : 0		—		A I	5) 8)
91.3	0 : 4		0 : 4		—		S II	3) 9)
80.3	0 : 2		0 : 2		—		S II	3) 5) 8?)
76.8	0 : 1		f : 1		—		S II	3) 5) 8?)
68.5	0 : 3		0 : 1		—		S III	3)10?)
57.4	2 : 6		1 : 7		—		S II	2) 9)
55.5	2 : 4		1 : 5		—		S II	2) 9)
50.6	0 : 3		0 : 2		—		S II	2) 9)
44.3	3 : 0		2 : 0		—		A I	5) 8)
36.3	0 : 3		0 : 1		—		S III	. 10)
33.2	1 : 0		f : 0		—		A I	5)
32.9	0 : 2		0 : 1		—		S II	. 10)
29.2	0 : 1		—		—		S III	. 10)
13.0	2 : 0		1 : 0		—		A I	5)
04.7	3 : 6		2 : 6		—		S II	2) 9)
00.4	0 : 2		0 : 1		—		S III	2)10)

1.....Tube I, w .....Wide, c .....Capillary.
2.....Tube II, W.....Weak, H.....Heavy.
3.....Spark, C .....Capacity, L.....Self-Induction.
A.....Arc Type, S.....Spark Type.
I: Are Line, II: Spark Line, III: Super-Spark Line, IV: Super-Super-Spark Line.

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
6195.5	0 : 3		0 : 2		—		S III	2)10)
91.6	2 : 0		1 : 0		—		A I	5) 8)
61.9	1 : 3		0 : 3		—		S II	2) 9)
49.0	1 : 3		f : 3		—		S III(?)	2)10)
32.9	0 : 1		0 : 1		—		S III	. 10)
27.4	3 : 8		3 : 8		—		S II	2) 9)
6086.8	0 : 2		0 : 1		—		S —	2)10)
84.7	0 : 3		0 : 3		—		S III	2) 9)
82.3	6 : 3		4 : 1		—		A I	5) 8?)
78.2	0 : 2		0 : 2		—		S II	. 9)
74.9	3 : 6		3 : 6		—		S II	2) 9)
68.8	1 : 4		1 : 5		—		S II	2) 9)
53.0	1 : 0		1 : 0		—		A I	5)
48.4	0 : 1		f : 1		—		S(?) —	5) 8?)
43.9	1 : 3		0 : 3		—		S II	. 10)
36.5	0 : 1		0 : 1		—		S —	5)10)
23.9	2 : 0		2 : 0		—		A I	5) 8)
15.8	0 : 3		0 : 2		—		S III	. 10)
07.6	0 : 2		0 : 1		—		S III	. 10)
5980.5	1 : 0		1 : 0		—		A I	5)
67.7	1 : 0		f : 0		—		A I	5)
50.1	6 : 10		5 : 10		—		S II	2) 9)
20.7	1 : 5		1 : 5		—		S II	2?) 9)
5893.8	5 : 4		4 : 3		—		A I	1) 5)8?)
75.1	0 : 2		0 : 1		—		S III	. 10)
32.7	1 : 0		1 : 0		—		A I	5)10)
30.0	0 : 3		0 : 2		—		S III	. 10)
19.6	1 : 4		0 : 4		—		S II	. 9)
5793.0	0 : 1		0 : f		—		S(?) —	5) 9)
87.1	1 : 6		0 : 6		—		S II	. 9)
80.4	1 : 0		1 : 0		—		A I	5)
74.7	6 : 10		5 : 10		f : 1		S II	2) 9)
64.3	3 : 1		3 : 0		—		A I	5) 9)
60.8	3 : 7		3 : 7		—		S II	2) 9)
39.5	5 : 10		6 : 12		f : 1.5		S II	2) 9)
38.5								2) 9)
10.43	4 : 10		5 : 10		f : 3		S II	2) 9)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
5702.07	1 : 4		1 : 5		—		S	II	2?) 9)
5690.96	4 : 10		4 : 10		f : 1		S	II	2) 9)
90.89									
79.9	0 : 1		0 : 2		—		S	—	. 9)
78.15	4 : 10		4 : 10		—		S	II	2) 9)
78.06									
73.7	0 : 3		0 : 1		—		S	III	. 10)
43.4	1 : 5		1 : 5		0 : f		S	II	. 9)
25.66	6 : 13		6 : 12		1 : 2		S	II	2) 9)
12.82	3 : 5		3 : 5		—		S	II	2) 9)
03.2	1 : 3		1 : 3		—		S	II	. 9)
00.21	3 : 6		3 : 6		0 : f		S	II	. 9)
5598.68	2 : 6		3 : 6		0 : f		S	II	2) 9)
98.55									
93.09	2 : 4		2 : 4		—		S	II	2) 9)
90.3	0 : 2		1 : 3		—		S	II	. 9)
86.3	3 : 1		3 : f		—		A	I	5) 8?)
68.7	0 : 3		0 : 3		—		S	II	. 9)
51.7	2 : 5		2 : 6		0 : 1		S	II	2) 9)
46.4	1 : 2		1 : 2		—		S	III	. 9)
22.1	2 : 4		3 : 6		—		S	II	2) 9)
04.77	4 : 8		4 : 8		f : 1		S	II	2) 9)
01.00	1 : 0		1 : 0		—		A	I	5)
5497.08	6 : 15		6 : 15		1 : 4		S	II	2) 9)
96.96									
.85									
.79									
.73									
93.45	1 : 8		1 : 8		0 : f		S	II	3) 9)
.05									
91.52	3 : 8		2 : 8		0 : f		S	II	3) 9)
79.55	1 : 5		0 : 5		—		S	II	. 9)
68.1	0 : 2		0 : 3		—		S	—	. 9)
64.77	8 : 20		8 : 20		2 : 4		S	II	2) 9)
57.1	1 : 4		1 : 4		—		S	II	.
49.0	0 : 1		0 : 1		—		S	III	. 10)
37.97	4 : 8		3 : 8		—		S	II	2) 9)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
5435.80	6 : 10		6 : 10		—		S II	2) 9)
27.4	3 : 2		: 2		—		A I	1) 5) 10)
22.71	2 : 5		1 : 5		—		S II	3) 9)
21.97	0 : 3		0 : 3		—		S II	. 9)
15.0	0 : 3		f : 3		—		S II	. 9)
11.7	0 : 1		0 : 1		—		S III	. 10)
07.35	6 : 12		6 : 12		0 : 2		S II	2) 9)
05.59 .38 .23 .11	6 : 16		6 : 14		1 : 3		S II	2) 9)
5380.1	1 : 4		f : 4		—		S II	2?) 9)
74.5	0 : 1		0 : 1		—		S(?) —	5) 8)
72.5	0 : 3		0 · 3		—		S II(?)	2?) 9)
69.75	4 : 10		4 : 10		0 : f		S II	2) 9)
67.5	0 : 3		1 : 4		—		S II	. 9)
56.0	0 : 1		1 : 2		—		S III	. 10)
51.9	0 : 2		1 : 3		—		S II	2?) 9)
49.7	0 : 3		0 : 3		—		S II	2?) 9)
45.17	6 : 18		6 : 18		f : 2		S II	2) 9)
38.20	6 : 18		6 : 18		f : 2		S II	2) 9)
26.4	1 : 4		1 : 4		—		S II	2?) 9)
22.71	3 : 5		3 : 5		—		S II	2) 9)
14.6	0 : 1		0 : 1		—		S III	. 10)
09.0	1 : 3		1 : 3		—		S III(?)	2) 10)
04.3	0 : 1		f : 2		—		S(?) —	5) 8?)
5299.68	2 : 5		2 : 5		—		S II	2) 9)
96.7	0 : 2		1 : 3		—		S II	2?) 9)
88.7	1 : 3		1 : 4		—		S II	. 9)
69.36	4 : 8		4 : 8		0 : f		S II	2) 9)
66.8	0 : 2		0 : 2		—		S II	. 9)
65.27 .15	3 : 6		3 : 6		—		S II	2) 9)
45.65	6 : 10		6 : 10		0 : f		S II	2) 9)
34.58	4 : 2		4 : 1		—		A I	1) 4) 5) 8)
28.93	2 : 5		2 : 5		—		S II	2?) 9)
16.22	4 : 9		4 : 9		—		S II	2) 9)

Table I. Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
5214.04	1 : 5		1 : 5		—		S II	2) 9)
05.5	0 : 3		0 : 4		—		S II	. 9)
04.08	3 : 1		4 : 0		—		A I	4) 5) 8)
5198.9	0 : 3		0 : 3		—		S III	2)10)
89.4	0 : 3		0 : 3		—		S II	. 9?)10)
86.3	1 : 0		—		—		A(?) —	5)
85.14	3 : 7		1 : 6		—		S II	3) 9)
78.1	2 : 4		1 : 4		—		S III	2)10)
61.20	8 : 30		10 : 30		1 : 3		S II	2) 9)
56.4	2 : 5		1 : 5		—		S II	3?) 9)
54.9	0 : 2		0 : 3		—		S II(?)	3?) 9)
49.7	2 : 5		2 : 5		—		S II	2?) 9)
47.4	1 : 4		1 : 4		—		S II	2) 9)
36.1	0 : 1		0 : 1		—		S II	5)
31.3	1 : 3		1 : 4		—		S II	2) 9)
24.6	0 : 1		0 : 3		—		S II	2) 9)
19.32	5 : 3		5 : 1		f : 0		A I	1) 4) 5) 8)
14.44	0 : 3		0 : 3		—		S III	2)10)
5098.8	0 : 1		0 : 1		—		S III(?)	.
68.2	0 : 1		0 : 1		—		S —	5) 8?)
65.5	3 : 6		3 : 6		—		S II	2) 9)
61.9	1 : 4		1 : 4		—		S II	2) 9)
57.4	0 : 1		0 : 1		—		S III	. 10)
48.1	0 : 1		0 : 1		—		S —	5)
46.4	2 : 4		2 : 4		—		S II	2) 9)
36.1	0 : 3		0 : 3		—		S III	. 10)
32.3	0 : 1		f : 1		—		S(?) —	5)
28.8	1 : 4		1 : 4		—		S II	. 9)
08.4	1 : 4		1 : 4		—		S II	. 9)
4992.2	1 : 3		0 : 3		—		S II	2)
86.95	4 : 10		4 : 8		0 : 2		S II	2) 9)
84.4	0 : 2		f : 3		—		S II	2)
74.5	0 : f		—		—		— —	5)
68.33	2 : 5		2 : 5		—		S II	2) 9)
65.7	0 : 2		0 : 3		—		S II	.
57.6	1 : 5		1 : 4		—		S II	3) 9)
43.1	2 : 5		1 : 4		—		S II	3) 9)

Table 3, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
4938.6	0 : 2		0 : 2		—		S III	.
29.9	0 : 3		0 : 2		—		S II	.
24.4	0 : 2		1 : 2		—		S II	.
16.94	6 : 4		6 : 2		f : 0		A I	1) 4) 5) 8)
10.3	0 : 3		0 · 3		—		S II	. 9)
08.5	0 : 3		0 : 3		—		S II	2) 9)
02.2	1 : 0		1 : 0		—		A I	5)
4896.72	4 : 3		4 : 1		—		A I	1) 5) 8)
91.3	0 : 3		0 : 2		—		S III	. 10)
87.7	1 : f		1 : f		—		A(?) —	5)
83.7	2 : 7		2 : 7		—		S II	2) 9)
81.6	1 : 5		1 : 4		—		S II	2) 9)
64.5	1 : 5		1 : 5		—		S II	. 9)
62.33	20 : 10		20 : 10		1 : 0		A I	1) 5) 8?)
53.1	1 : 4		f : 4		—		S II	3?) 9)
50.4	4 : 10		4 : 10		—		S II	2) 9)
35.1	2 : 5		2 : 5		—		S II	3?) 9)
28.3	3 : 6		3 : 6		—		S II	2) 9)
08.0	0 : 4		f : 4		—		S II	2?) 9)
06.4	3 : 6		4 : 6		—		S II	2) 9)
4799.8	0 : 1		0 : 1		—		S III	2?) 10)
90.9	1 : 3		1 : 3		—		S II	3?) 9)
88.2	1 : 4		2 : 4		—		S III	2) 9)
87.2	1 : 4		1 : 5		—		S II	2?) 9)
82.5	—		f : 0		—		A(?) —	5)
75.8	0 : 1		0 : 1		—		S II	5) 9)
73.1	0 : f		0 : f		—		S III	5) 10)
68.2	1 : 6		1 : 7		—		S III&II	3?) 9)
65.7	0 : 5		0 : 5		—		S II	. 9)
63.4	5 : 6		5 : 6		—		A&S I&II	2) 9)
52.7	1 : 4		1 ; 4		—		S II	2) 9)
42.9	1 : 3		1 : 3		—		S II	. 9)
37.1	0 : 1		0 : 1		—		S II	.
30.5	2 : 6		2 : 6		—		S III&II	3) 9)
26.3	1 : 2		2 : 3		—		S II	5) 8?)
22.1	1 : 2		1 : 2		—		S II	5)
11.7	1 : 4		1 : 4		—		S II	. 9)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
4707.9	1 : 4		1 : 4		—		S II	. 9)
02.5	0 : 2		1 : 3		—		S II	. 9)
00.8	1 : 0		1 : 0		—		A —	.
4691.1	0 : 2		0 : 1		—		S —	5)
* 90.62	1 : f		2 : 1		—		A I	. 8?)
87.3	0 : 3		1 : 3		—		S —	5) 8?)
76.5	3 : 8		2 : 8		—		S II	3)
75.5	6 : 10		6 : 12		0 : f		S II	2) 9)
66.5	5 : 12		6 : 12				S II	3) 9)
63.8	1 : 3		0 : 3		—		S III	3) 10)
57.4	1 : 5		2 : 5		—		S II	3) 9)
40.7	4 : 10		4 : 8		f : 2		S II	3) 9)
34.8	0 : 4		0 : 4		—		S III	3) 10)
32.4	6 : 10		5 : 10		f : 2		S II	2) 9)
22.11	4 : 6		4 : 6		—		S II	3) 9)
11.46	2 : 5		1 : 5		—		S II	2) 9)
00.04	3 : 6		3 : 6		—		S II	3)
4597.05	0 : 3		0 : 3		—		S III	3) 9)
91.19	2 : 4		2 : 4		—		S II	3) 9)
86.85	2 : 4		1 : 4		—		S II	3) 9)
80.13	0 : 3		1 : 3		—		S III	2) 10)
76.82	2 : 6		2 : 5		—		S II	3) 9)
74.44	2 : 8		1 : 6		—		S II	3) 9)
71.68	0 : 3		f : 3		—		S II	2) 9)
60.99	1 : 3		f : 3		—		S II	2) 9)
58.16	0 : 3		0 : 3		—		S III	2) 10)
44.26	2 : 5		2 : 5		—		S II	3) 9)
40.94	1 : 3		1 : 3		—		S II	2) 9)
28.29	0 : 4		0 : 3		—		S III	2) 10)
12.80	0 : 5		0 : 4		—		S III	2) 10)
4499.86	f : 5		1 : 4		—		S II	3?) 9)
96.21	f : 5		1 : 4		—		S II	. 10)
95.94					—			. 9)
88.82	1 : 8		2 : 6		0 : f		S II	2) 9)
87.69	0 : 3		f : 3		—		S II	. 9)
81.11	0 : 2		f : 3		—		S —	2?) 10)
* 78.60	3 : 2		4 : 2		—		A I	. 9)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities					Types	Remarks
	1		2		3		
	w	c	W	H	C+L	C	
4476.22	f : 10		3 : 8		—	S II	3) 9)
73.69	2 : 12		5 : 10		0 : 1	S II	2) 9)
64.58	3 : 12		4 : 9		0 : 1	S II	2) 9)
63.05	2 : 5		1 : 4		—	S II	2) 9)
58.66	f : 5		1 : 4		—	S II	3?) 9)
56.87	2 : 8		2 : 7		0 : f	S II	2?) 9)
53.17	3 : 18		6 : 18		0 : 1	S II	3) 9)
51.39	f : 3		f : 2		—	S II	2?) 9)
46.96	1 : 8		4 : 8		0 : f	S II	3?) 9)
45.04	2 : 12		6 : 12		0 : 1	S II	3) 10)
42.84	2 : 8		4 : 7		0 : f	S II	2) 9)
34.43	0 : 1		0 : 3		—	S III	3) 10)
31.89	0 : 1		f : 3		—	S III	3) 10)
28.41	1 : 8		5 : 8		—	S II	3) 9)
23.98	2 : 12		8 : 12		0 : f	S II	3) 9)
22.27	1 : 5		3 : 6		—	S II	3) 9)
17.47	f : 3		f : 4		—	S II	. 9)
16.95	f : 8		3 : 8		—	S II	3?) 9)
12.62	2 : 5		4 : 8		—	S II	3) 9)
10.26	3 : 15		8 : 15		0 : f	S II	3)
* 07.83	2 : 1		3 : 2		—	A I	.
04.60	0 : 3		1 : 3		—	S II	. 9)
03.72	3 : 6		4 : 6		0 : f	S II	2) 9)
4399.15	2 : 6		5 : 8		—	S II	3) 9)
94.83	0 : 3		1 : 3		—	S III	. 9)
88.77	f : 5		2 : 4		—	S II	2) 9)
76.34	3 : 8		6 : 10		—	S II	3) 9)
62.62	f : 6		3 : 6		—	S II	3) 9)
42.25	2 : 7		6 : 10		0 : f	S II	3) 9)
22.92	1 : 5		2 : 6		0 : f	S II	3?) 9)
* 21.92	8 : 5		9 : 5		f : 0	A I	. 9)
17.25	f : 4		1 : 4		—	S III	2)
4296.51	f : 7		2 : 6		—	S II	3) 9)
92.14	1 : 7		3 : 8		—	S II	3) 9)
88.32	f : 6		0 : 3		—	S II	2) 9)
82.12	f : 7		2 : 6		—	S II	3) 9)
73.75	0 : 2		0 : 1		—	S —	.

Table I, Iodine (continued)

	Wave-lengths	Relative Intensities						Types		Remarks
		1		2		3				
		w	c	W	H	C+L	C			
	4271.75	0	4	1	4	—		S	II	2?)10)
	63.91	0	4	f	4	—		S	III	2?)10)
	60.32	0	4	f	3	—		S	II	. 9)
	59.18	0	4	f	4	—		S	III	2?)10)
	40.81	0	6	f	3	—		S	II(?)	2?) 9)
	35.65	6	15	6	15	0	f	S	II	2) 9)
*	34.59	1	f	2	1	—		A	I	. 9)
	25.65	2	5	3	6	—		S	II	2) 9)
	23.54	0	3	f	4	—		S	II	2?)10)
	21.24	f	5	4	7	—		S	III	2)10)
	19.43	f	7	3	6	—		S	II	. 9)
*	08.98	1	0	1	f	—		A	I	.
	4174.02	2	6	3	8	—		S	II	2) 9)
	70.57	0	3	f	4	—		S	III	2,10)
*	48.37	4	3	5	3	—		A	I	.
	45.87	0	2	0	2	—		S	III	2)10)
	38.14	0	4	0	3	—		S	III	2) 9)
	36.45	0	3	0	4	—		S	III	2)10)
*	34.11	5	2	6	3	—		A	I	.
	33.38	0	3	0	2	—		S	III	2)10)
*	29.15	8	5	9	5	—		A	I	.
	28.85	0	5	2	5	—		S	III	2)10)
	26.30	0	2	0	2	—		S	III	. 9)
	20.46	0	2	0	1	—		S	III	.
	20.15					—				. 9)
	16.80	0	2	0	2	0	f	S	II	. 9)
	08.39	0	3	0	3	f	1	S	III	2)10)
	03.22	1	3	0	3	1	2	S	II	.
	03.09									. 9)
	4093.60	0	3	0	3	—		S	III	2)10)
	70.87	f	5	f	5	2	3	S	III	2)10)
	56.32	0	2	0	3	0	1	S	III	2)10)
	49.96	0	3	0	3	f	1	S	III	2)10)
	44.01	f	3	f	2	f	1	S	II	2) 9)
	42	0	2	0	2	f	1	S	III	. 10)
	36.20	1	3	1	4	1	2	S	II(?)	2) 9)
	32.14	0	3	0	3	f	1	S	III	2)10)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
4025.16	0 : 4		0 : 3		f : 1		S	III	2)10)
17.44	0 : 3		0 : 2		0 : f		S	III	2) 9)
14.15	0 : 2		0 : 2		—		S	II	.
3984.05	f : 5		f : 5		2 : 3		S	III	2)10)
72.99	f : 2		1 : 5		1 : 2		S	II	2?) 9)
65.89	1 : 4		1 : 5		1 : 2		S	II	2) 9)
63.60	0 : 3		0 : 2		f : 1		S	III	.
63.26									. 11)
54.28	0 : 1		0 : 1		—		S	—	.
50.08	0 : 3		0 : 3		f : 1		S	III	2)10)
42.52	1 : 3		f : 2		—		S	III	. 9)
40.22	1 : 6		1 : 8		4 : 6		S	III	2)10)
38.29	0 : 3		0 : 3		f : 1		S	III(?)	2)10)
37.37	1 : 2		1 : 3						2?) 9)
31.25	2 : 7		1 : 7		4 : 5		S	III	2)10)
24.34	0 : 2		0 : 2		0 : f		S	II(?)	. 9)
15.35	f : 3		f : 3		f : 1		S	II	. 9)
12.70	0 : 3		0 : 4		f : 1		S	III	2)10)
07.50	1 : 3		1 : 2		f : 1		S	II	2) 9)
05.95	0 : 3		0 : 2		f : 1		S	III	2)10)
01.33	f : 1		f : 1		—		S	II	2) 9)
3897.51	1 : 5		1 : 6		4 : 5		S	III	2)10)
93.19	1 : 3		1 : 3		f : 1		S	II	2) 9)
77.40	f : 2		f : 2		0 : f		S	III(?)	2) 9)
75.94	0 : 3		0 : 3		0 : f		S	III(?)	2)10)
72.15	0 : 1		0 : 1		—		S	II	2) 9)
51.04	f : 3		0 : 4		1 : 2		S	II	2) 9)
43.17	f : 3		f : 3		0 : f		S	II(?)	2) 9)
41.21	0 : 1		f : 1		—		S	—	. 9?)
38.47	0 : 3		0 : 3		0 : f		S	III	2)10)
33.82	f : 3		1 : 4		f : 1		S	II	2) 9)
21.62	f : 5		1 : 5		2 : 3		S	III	2)10)
08.36	1 : 6		1 : 6		3 : 4		S	III	2)10)
03.70	0 : 3		f : 3		—		S	III	. 10)
01.69	0 : 1		f : 2		—		S	—	.
00.07	0 : 2		0 : 3		0 : f		S	III	.
3793.72	0 : 1		f : 2		—		S	III	. 9)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
3789.55	o : f		o : 1		—		S —	.
81.81	f : 3		1 : 3		o : f		S III	2)10)
79.54	f : 3		f : 4		o : f		S II(?)	. 10)
79.19								2) 9)
74.04	o : 4		o : 3		o : f		S III	2?)10)
71.19	o : 1		f : 2		—		S —	. 9)
54.76	o : 3		o : 3		—		S IV	2)11)
42.38	1 : 3		2 : 3		1 : 2		S II(?)	2) 9)
42.03	o : 2		o : 3				S III(?)	.
34.54	f : 2		f : 3		1 : 2		S II	. 9)
31.23	o : 1		f : 2		—		S II	2)
27.44	o : f		f : 2		o : f		S III(?)	.
25.02	f : 4		f : 5		1 : 2		S III	2)10)
16.52	f : 1		1 : 3		o : f		S II	2)
11.66	o : 3		f : 4		f : 1		S III	2?)10)
10.16	f : 1		1 : 2		o : f		S II	.
09.71								2) 9)
02.29	o : 2		o : 3		o : f		S III	2?)10)
3696.56	o : f		f : 1		—		S II	3?)
95.92	o : f		o : f		—		S —	. 9)
92.49	o : f		f : 2		o : f		S II	2) 9)
88.48	f : 4		f : 5		2 : 3		S III	2)10)
86.79	f : 4		f : 5		2 : 3		S III	2)10)
78.90	o : 2		o : 2		o : f		S III	2)10)
61.99	f : 3		1 : 4		f : 1		S II	2) 9)
57.34	f : 2		1 : 3		f : 1		S II	2) 9)
51.05	o : f		o : 1		—		S II	. 9)
38.01	o : 2		o : 3		o : f		S III	2)10)
27.72	o : f		o : 1		o : f		S II	. 9)
27.00	o : f		o : 1		—		S —	2) 9)
16.10	o : f		o : 1		o : f		S II(?)	2) 9)
14.02	o : f		o : 1		—		S IV	2)11)
07.76	o : 2		o : 3		f : 1		S III	2)10)
03.27	o : f		o : 1		—		S II	2)
00.88	o : f		o : 1		—			.
00.71					—		S III(?)	.
00.48	o : f		o : 1		o : f			2)10)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
3583.45	0 : 3		f : 4		1 : 2		S III	2)10)
75.94	0 : f		f : 2		0 : f		S II	2) 9)
73.78	0 : 1		f : 2		0 : f		S II	2) 9)
61.47	0 : 3		f : 5		f : 1		S III	. 10?)
61.32								2)10)
58.26	0 : f		0 : 1		—		S II	2) 9)
52.51	0 : f		f : 2		0 : f		S II	3) 9)
47.07	0 : f		0 : 1		—		S IV	2)11)
36.29	0 : f		0 : 1		—		S II	. 10)
36.15								2) 9)
33.66	0 : f		0 : 1		—		S II	2) 9)
27.12	0 : 1		f : 3		0 : f		S II	2) 9)
26.55	0 : f		0 : 1		—		S II	. 9)
16.17	0 : f		0 : 1		—		S II	2) 9)
12.82	0 : 1		0 : 2		0 : f		S III(?)	2)10)
11.64	0 : f		0 : 1		—		S —	. 9)
3498.15	2 : 6		1 : 10		2 : 3		S III	2)10)
84.10	0 : f		0 : 2		f : 1		S II	2)
81.97	1 : 5		f : 9		2 : 3		S III	2)10)
74.21	0 : 1		0 : 2		0 : f		S III	3?)10)
61.16	1 : 3		0 : 8		1 : 2		S III	2)10)
47.81	0 : 1		0 : 1		0 : f		S II	2) 9)
35.16	0 : 1		0 : 1		0 : 1		S II	2) 9)
26.58	—		0 : 1		—		S —	2) 9)
25.09	1 : 3		0 : 3		f : 2		S II(?)	2) 9)
14.03	0 : 2		0 : 4		f : 1		S III	2)10)
01.61	0 : f		0 : 1		—		S II	2) 9)
3384.08	0 : f		0 : 1		—		S II	2) 9)
82.02	0 : 2		0 : 4		f : 1		S III	2)10)
77.78	0 : f		0 : 1		—		S III	3)10)
74.82	0 : 1		0 : 4		f : 1		S II(?(	2)10)
60.16	0 : f		0 : 2		f : 1		S II	2) 9)
54.71	0 : f		0 : 1		—		S —	.
50.26	1 : 4		1 : 8		1 : 2		S III	2)10)
42.63	1 : 3		1 : 9		1 : 2		S III	2)10)
26.58	0 : 1		0 : 1		—		S II	2)10
23.65	0 : 1		0 : 1		—		S III	3?)10)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
3321.74	0 : 1		0 : 2		0 : f		S III	2)10)
18.24	0 : f		0 : 1		—		S II	2) 9)
03.17	2 : 8		2 : 10		4 : 6		S III	2)10)
02.55							S II(?)	2) 9)
00.63	0 : 2		0 : 4		f : 1		S IV	2)11)
3295.88	0 : 1		0 : 2		—		S III	. 10)
89.01	0 : 2		0 : 5		6 : 8		S III(?)	2) { 9) 10)
88.44	2 : 10		1 : 16				S III	
75.11	1 : 8		0 : 10		4 : 6		S III	2)10)
73.77	0 : 1		0 : 3		—		S III	3?).
73.4					—			. 10)
66.91	0 : 1		0 : 2		0 : f		S III	2)10)
56.58	1 : 2		0 : 3		f : 1		S II	2) 9)
53.95	0 : 1		0 : 3		f : 1		S III	2)10)
44.41	0 : 1		0 : 1		—		S III	3?)10)
35.78	0 : 2		0 : 3		f : 1		S III	. 10)
30.59	1 : 4		0 : 6		2 : 3		S III	2)10)
30.06							S III	2)10)
25.06	0 : 1		0 : 3		0 : f		S IV	2)11)
13.76	0 : 1		0 : 4		f : 1		S III	2)11)
09.71	0 : 1		0 : 3		f : 1		S II	. 9)
00.56	0 : 1		0 : 2		0 : f		S III	2)10)
3195.23	0 : 1		0 : 2		—		S III(?)	. 10)
94.11	1 : 6		1 : 8		4 : 6		S IV	2)10)
86.28	0 : f		0 : f		—		S II	. 9)
81.81	0 : 3		0 : 6		2 : 3		S IV	2)11)
75.29	1 : 2		1 : 3		f : 1		S II	2) 9)
73.36	0 : f		0 : f		—		S II(?)	3?)10)
69.83	0 : f		0 : 1		0 : f		S IV(?)	. 9)11)
61.07	0 : 1		0 : 1		0 : f		S II	. 9)
57.34	0 : 1		0 : 2		f : 1		S II	2)10)
54.48	0 : 3		0 : 4		1 : 2		S IV	.
54.16								2)11)
49.83	f : 2		0 : 3		1 : 2		S III	2)
39.91	1 : 4		0 : 4		2 : 3		S III	3)10)
36.71	f : 1		0 : 1		1 : 2		S II	2) 9)
17.85	f : 2		f : 3		1 : 2		S II	2) 9)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
3113.27	f	2	0	3	0	1	S	III	3)10)
06.73	0	1	0	1	0	f	S	II	2) 9)10)
03.84	1	2	0	2	f	1	S	III	3)10)
3091.08	1	4	0	5	1	2	S	III	3?)
90.11	—		f	0	—		A(?)	—	.
88.35	1	3	0	5	1	2	S	III	3?)10)
83.00	0	2	0	4	1	2	S	III	3)10)
81.81	2	4	f	4	2	3	S	III	2) 9?)10)
78.91	3	4	3	3	3	4	S(?)	II(?)	2) 9)
78.00	1	3	0	6	1	2	S	III	3)10)
74.00	0	2	0	3	f	1	S	III	3)10)
73.65									3)
72.55	0	f	0	1	—		S	II(?)	3) 9)10)
69.47	0	1	0	2	0	f	S	III	2)11)
68.37	0	1	0	2	0	f	S	II	3)
64.11	0	2	f	4	f	1	S	III	3)
55.35	2	7	f	8	5	7	S	III	2)10)
38.56	1	3	0	7	2	3	S	III	2)10)
33.42	0	2	0	4	f	1	S	III	2)10)
30.53	1	4	0	6	1	2	S	III	2)10)
21.2	1	4	1	5	3	5	S	II(?)	2)6)9)10?)
19.9	0	f	0	2	—		S	III(?)	. 10)
18.04	—		0	1	—		S	III	3)10)
15.5	0	2	0	4	1	2	S	III	2)10)
13.2	0	1	0	3	—		S	III	3)10)
12.6									3) 9)
06.9	—		0	1	0	2(?)	S	III	3?)10)
04.76	0	2	0	2	0	2	S	IV	.
00.6	0	2	0	3	0	3	S	III	2) 9)10)
2993.8	2	6	1	5	3	6	S	II	2) 6) 9)
92.6	0	1	0	2	—		S	III	. 10)
91.39	—		0	2	—		S(?)	III	. 10)
88.4	0	4	0	5	1	2	S	III	2) 6)10)
83.3	0	5	f	5	2	4	S	III	3)10)
79.0	0	1	0	2	1	2	S	II	3)10)
78.1	0	2	0	3	1	2	S	III	2)10)
73.7	0	2	0	2	1	2	S	III	3)10)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
2970.74	0 : 5		f : 7		3 : 6		S II	. 9)
69.92							S III	2)10)
58.3	1 : 9		2 : 12		8 : 12		S III	2) 6)10)
57.5							S II	2) 9)
56.2							S II	2) 9)
54.3	0 : 1		0 : 2		0 : 1		S III	2)10)
51.0	0 : 1		0 : 1		—		S III	. 10)
49.0	0 : 7		f : 6		4 : 6		S III	3) 6)10)
42.4	0 : 1		f : 3		—		S II	. 6) 9)
41.6					—		S III	. 10)
37.1	0 : 2		1 : 4		1 : 2		S III	6)10)
36.9								.
34.1	0 : 1		0 : 1		—		S III	3)10)
31.7	1 : 5		2 : 4		1 : 2		S II(?)	2) 6) 9)
30.2	—		0 : 1		0 : 1		S II	. 10)
28.42	0 : 1		0 : 2		0 : 1		S III	2)10)
25.0	0 : 1		f : 2		1 : 2		S II	2) 6) 9)
22.7	0 : 1		0 : 2		0 : 1		S III	. 10)
17.7	0 : 5		0 : 6		3 : 5		S IV	2) 6)10)
15.8	0 : f		0 : 1		0 : f		S II	. 9)10)
06.54	0 : 3		0 : 3		—		S IV(?)	3) 6)10)
02.9	0 : 1		0 : 1		0 : 1		S II	2) 9)
2883.0	0 : 2		0 : 3		1 : 3		S II	2)10)
82.6							S III	6) 9)
78.6	3 : 12		3 : 8		5 : 8		S II	3) 6) 9)
72.8	0 : 6		0 : 5		2 : 6		S III	3) 6)10)
68.7	0 : 2		0 : 3		1 : 2		S III	2)10)
61.8	0 : 1		0 : 2		—		S II	3) 9)
57.5	—		0 : 1		—		S II	. 9)
47.5	f : 4		1 : 6		1 : 3		S III	3)10)
46.9							S II	6) 9)
36.9	0 : 6		0 : 7		2 : 10		S III	6)10)
32.87	0 : 2		0 : 3		f : 2		S III	2)10)
24.8	0 : 3		0 : 3		0 : 1		S III	3) 6)10)
10.0	0 : 3		0 : 3		1 : 3		S III	2)10)
08.5	2 : 6		1 : 5		3 : 6		S II	2) 9)
04.7	—		0 : 1		—		S II	. 9)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
2799.65	o : 4		f : 5		o : 1		S	III	3)10)
93.5	o : 1		o : 1		—		S(?)	—	2)10)
90.44	o : 1		o : 2		—		S	III	3)10)
89.4	f : 3		f : 3		2 : 4		S	III	3) 6)10)
80.3	o : 1		o : 2		o : 1		S	III(?)	3)10)
76.1	o : 1		o : 2		o : 1		S	III	3?)10)
74.8	o : 2		o : 2		o : 1		S	III	2?)10)
71.9	o : 3		o : 3		1 : 2		S	III	3?)10)
70.7	o : 1		o : 1		—		S(?)	III	. 9)
65.6	2 : 5		1 : 4		1 : 2		S	IV	3) 6) 9)
65.1							S	II	. 9)
63.2	o : 1		o : 3		o : 1		S	III	2?)10)
59.2	o : 3		o : 4		f : 2		S	III	3)10)
54.7	—		o : 1		—		S	III	2)10)
53.5	o : 1		o : 2		—		S	II(?)	. 9)
51.5	o : 2		o : 3		o : 1		S	III	. 10)
46.50	o : 1		o : 2		1 : 2		S	II	2) 9)
44.45	o : 1		o : 1		—		S	II	2) 9)
38.39	o : 1		o : 2		—		S	III	2)10)
37.46	o : 2		o : 2		o : f		S	III	2)10)
32.2	o : 1		o : 1		—		S(?)	II(?)	. 10)
31.8					—				.
30.1	3 : 8		3 : 8		6 : 10		S	II	2) 6) 9)
24.1	o : 2		o : 3		1 : 2		S	III	2)10)
23.04	o : 1		o : 1		—		S	II	. 9)
19.70	o : 1		o : 2		o : 1		S	II	. 9)
12.2	3 : 7		1 : 6		4 : 8		S	II	2) 6) 9)
08.1	f : 4		f : 3		1 : 2		S	II	2) 9)
05.3	o : 3		f : 3		—		S	III	3)10)
04.5	o : 1		o : 1		—		S	II	. 9)
01.4	f : 3		1 : 3		o : 1		S	II	2) 6) 9)
2698.3	2 : 5		f : 3		1 : 3		S	II	2) 6) 9)
90.44	o : 1		o : 2		o : 1		S	III	2)10)
88.9	4 : 10		3 : 6		7 : 15		S	II	2) 9)
88.5							S	—	. 6)
74.8	3 : 8		3 : 6		5 : 10		S	II	2) 6) 9)
71.2	o : 1		o : 1		—		S	II(?)	2) 9)

Table I, Iodine (continued)

Wave lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
2665.24	f : 2		f : 2		—		S II	. 9)
61.2	o : 1		o : 3		o : 1		S III	. 10)
60.7							S III	2)10)
59.2	o : 1		o : 1		—		S III	2)10)
55.77	o : 1		o : f		—		S II	. 9)
43.3	o : 2		o : 2		—		S III	. 10)
41.3	o : 1		o : 1		—		S III	. 9)
36.7	2 : 5		2 : 5		2 : 5		S II	3?) 6) 9)
36.2							S II	3?) 9)
32.0	—		o : 1		—		S II	. 9)
25.0	o : 3		o : 3		—		S III	2)10)
22.9	o : 1		o : 2		—		S III	2)10)
19.84	o : f		o : 1		—		S II	2) 9)
17.5	o : f		o : 1		f : 1		S III	2)10)
14.69	o : 3		o : 5		1 : 3		S IV(?)	2) 6)10)
12.9	o : 1		o : 1		—		S II	. 9)
10.69	2 : 5		2 : 5		3 : 5		S II	2) 9)
07.3	f : 3		f : 2		1 : 2		S II	2) 9)
05.6	o : 2		o : 3		f : 1		S III	10)
05.5								2) 6)
03.6	—		o : 1		—		S II	2) 9)
2596.5	o : f		o : 1		—		S III	2)10)
93.4	5 : 12		4 : 8		6 : 10		S II	2) 6)10)
91.04	o : 1		o : 2		o : 1		S III	2)10)
88.6	2 : 6		2 : 6		2 : 4		S II	2) 6) 9)
88.09							S II	2) 9)
86.7	2 : 5		2 : 5		2 : 4		S II	2) 6) 9)
84.8	o : 1		o : 2		o : 1		S II	9)
84.7								2)
82.7	8 : 18		5 : 8		8 : 15		S II	2) 6) 9)
81.57	f : 2		o : 2		o : 1		S III	2)10)
80.71	f : 2		o : 2		—		S III	2)10)
75.5	o : 2		o : 5		1 : 2		S III	2)10)
67.48	o : 3		o : 6		o : 3		S III	2) 6)
66.2	6 : 15		4 : 16		6 : 10		S II	2) 6)
64.34	2 : 5		2 : 5		2 : 4		S II	2) 6) 9)
62.4	2 : 4		2 : 4		o : 1		S II	3?) 6) 9)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
2559.7	f : 2		f : 3		0 : 1		S II	2) 9)
59.2							S II	.
57.64	0 : f		0 : f		—		S II	.
54.9	0 : f		0 : 2		—		S III	. 9)
52.41	0 : 1		0 : 2		—		S III	2)
46.7	—		0 : 1		—		S IV	. 10)
42.1	0 : 1		0 : 1		—		S II	. 9?)
40.1	0 : f		f : 1		—		S II	. 9)
37.56	0 : 2		0 : 3		—		S III	2) 11)
34.5	f : 2		f : 2		0 : 1		S II	6) 9)
34.2								9)
33.57	2 : 6		1 : 4		2 : 4		S II	2) 9)
30.94	1 : 3		f : 2		0 : 1		S II	2) 9)
27.7	—		0 : 1		—		S III	. 10)
27.3					—		—	. 10)
26.9	f : 4		f : 5		1 : 2		S III	2) 10)
26.6								. 10)
15.0	0 : 1		0 : 1				S II	. 9)
03.6	2 : 6		1 : 4		1 : 3		S —	. 9?)
02.97							S II	2) 9)
2499.6	1 : 4		1 : 4		1 : 3		S III	2) 10)
99.3							S II	2) 9)
94.71	2 : 6		1 : 4		1 : 3		S II	2) 6) 9)
91.61	1 : 3		f : 3		0 : 2		S II	2) 6) 9)
89.8	—		0 : f		—		S II	. 9)
89.1	0 : 2		f : 3		0 : 1		S IV	6) 11)
89.0							—	9)
84.6	0 : 2		0 : 3		0 : f		S III	2) 10)
82.0	—		0 : 1		—		— III	. 9) 10)
71.3	f : 2		f : 2		—		S II	. 9)
69.2	0 : 1		0 : f		—		S II	. 9) 10)
66.7	0 : 1		0 : 1		—		S III	. 11)
65.0							S —	. 10)
64.7	3 : 8		2 : 6		2 : 6		S III	2) 6) 9)
64.1							S II	. 9)
61.1	1 : 4		f : 4		2 : 3		S II	2) 9)
57.3	0 : 1		0 : 2		—		S III	2) 10)

Table I, Iodine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
2454.5	f : 1		f : 2		o : f		S II	2) 9)
50.4	—		o : 2		o : f		S III	. 10)
48.5	o : 1		o : f		—		S II	. 9)
47.8	f : 2		f : 2		1 : 2		S III	3?) 10)
44.19	f : 3		f : 3		1 : 2		S II	3?) 9) 10)
38.3					—		S II	. 9)
37.9	o : 1		f : 2		—		S —	. 9)
37.6					—		S III	2) 10)
36.20	o : 2		o : 2		o : f		S III	2) 10)
30.92	o : 2		o : 2		—		S III	. 10)
26.2	—		o : 1		—		S IV	. 11)
23.5	o : 1		o : 2		1 : 2		S III	3?) 10)
23.3								10)
22.35	o : 1		o : 2		—		S III	3?) 10)
19.5	2 : 5		2 : 6		2 : 4		S II	2) 10)
19.3								2) 9)
12.51	o : 2		f : 2		1 : 2		S II	3) 9)
11.9	o : f		o : 1		—		S III	. 10)
08.0	f : 3		f : 3		f : 1		S II	2) 9)
04.08	o : 2		o : f		—		S IV(?)	.
2398.2	o : 1		o : 1		—		S II	. 9)
97.25	f : 1		f : 1		—		S II	. 9)
84.95	o : 4		o : 5		o : 2		S II	. 9)
72.2	o : 5		f : 5		1 : 4		S II(?)	. 9)
61.3	o : 3		o : 3		f : 2		S III	. 10)
48.47	f : 2		f : 1		o : f		S II	2) 9)
46.25	o : 3		o : 3		o : 1		S II	2) 9)
44.5	2 : 5		2 : 3		—		S III	. 10)
44.3					—			2?) 10)
42.38	o : 1		o : 2		—		S II	2) 9)
35.5	f : 3		f : 2		o : 2		S II	2) 9)
34.13	f : 1		f : 1		—		S II	2) 9)
31.6	f : 2		f : 2		o : 1		S II	2) 9) 10)
28.4	o : 1		o : 2		o : 1		S III	2) 10)
27.4	—		o : 1		o : f		S III(?)	. 10)
20.3	f : 2		f : 2		—		S II	. 9)
2062.1	20 : 3		20 : 3		f : o		A I	7)
1876.4	12 : 2		12 : 2		—		A 1	7)
44.5	16 : 3		16 : 3		—		A I	7)
30.4	15 : 3		15 : 3		—		A I	7)

Notes:— 1) The first type of modes of broadening.
2) The second type of modes of broadening.
3) The third type of modes of broadening.
4) Lines disappeared when a capacity was put in the discharge circuit. (Goldstein).
5) Lines sorted out as arc type. (Wood and Kimura).
6) The wave-lengths of these lines were measured also by Cario and Oldenberg. (ZS. f. Phys., **31**, 919 (1925)).
7) The wave-lengths of these lines were measured by Turner.
8) Lines classified as I I. (L. and E. Bloch).
9) Lines classified as I II. (L. and E. Bloch).
10) Lines classified as I III. (L. and E. Bloch).
11) Lines classified as I IV. (L. and E. Bloch).

Table II, Bromine

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
6632.02	2 : 0		4 : 3		2 : 1		A I	4) 7) 9)
6582.52	f : 0		3 : 1		2 : 1		A I	9)
60.17	1 : 0		3 : 1		2 : 0		A I	1) 4) 7) 9)
45.00	1 : 0		3 : 1		2 : f		A I	4) 9)
6353.07	6 : 1		8 : 5		4 : 3		S III(?)	2)10)
51.02							A I	1) 4) 7) 9)
6204.36	f : 0		3 : f		—		A I	4)
6178.72	f : 0		4 : f		—		A I	.
70.09	f : 1		0 : 2		—		S II	2)
59.60	f : 0		3 : 1		—		A I	4)
49.95	4 : f		7 : 6		3 : 2		A I	1) 4) 7)
42.02	1 : 2		0 : 3		—		S II	2)
23.49	f : 0		5 : 2		—		A I	.
18.89	f : 2		0 : 4		—		S II	2)
6097.05	f : 0		2 : f		—		A I	.
5950.70	2 : 0		3 : 1		—		A I	.
40.83	f : 0		3 : f		—		A I	7)
5871.97	1 : 3		f : 4		—		S II	2)10)
68.40	0 : f		0 : 1		—		S II	2)10)
64.55	0 : f		f : 2		—		S II	2)10)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
5852.40	2	0	5	2	f	0	A	I	4) 7) 9)
33.71	f	0	3	0	—		A	I	.
31.04	4	6	3	5	—		S	II	2)10)
5719.17	1	3	f	4	—		S	II	10)
16.50	f	0	1	f	—		A(?)	—	.
11.25	2	3	1	4	—		S	II	10)
5657.83	0	1	0	2	—		S	II	2)10)
27.5	2	f	2	f	—		A	I	1)
22.38	1	2	1	2	—		S	—	10)
21.95					—			II	10)
00.90	f	1	1	2	—		S	II	2)10)
5590.15	8	10	2	5	f	3	S	II	2)10)
88.40			0	3			S	II	3)
45.91	0	1	0	2	—		S	II	2?)10)
36.52	f	0	3	f	—		A	I	.
29.19	f	0	2	0	—		A	I	.
16.87	0	f	0	2	—		S	II	2)10)
11.04	0	f	0	2	—		S	—	.
08.49	2	5	1	3	0	f	S	II(?)	2)10)
06.97	3	6	2	4	0	f	S	II	2)10)
5495.24	4	7	1	6	f	2	S	II	2)10)
89.00	3	6	1	6	f	1	S	II	2)10)
83.20	0	f	0	f	—		S	II	.
81.41	f	1	f	2	—		S	—	2)
80.20	0	f	0	1	—		S	II	
66.43	3	1	4	1	—		A	I	1) 4) 7)
50.28	f	0	2	0	—		A	I	1)
42.55	2	3	f	4	—		S	II	2)10)
35.30	2	4	f	5	—		S	II	2)10)
33.49	f	1	f	2	—		S	II	10)
25.21	2	4	1	6	f	1	S	II	2)10)
23.01	4	6	1	6	f	2	S	II	2)10)
5395.69	2	0	4	2	—		A	I	4) 7) 9)
70.51	1	0	2	f	—		A	I	.
64.38	f	0	2	f	—		A	I	1)
60.99	f	1	f	2	—		S	II	2)
45.53	3	1	3	1	f	0	A	I	4) 7) 9)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities				Types		Remarks
	1		2		3			
	w	c	W	H	C+L	C		
5335.30	o : f		o : 2		—		S II	2?)
32.18	8 : 12		5 : 8		f : 5		S II	2) 8)10)
04.31	5 : 8		3 : 7		f : 2		S II	2) 8)10)
5272.89	2 : 3		1 : 4		o : f		S II	2)10)
63.68	2 : 4		1 : 4		o : f		S II(?)	2)10)
39.99	1 : 4		o : 3		—		S II	10)
38.47	8 : 12		5 : 10		1 : 6		S II	2) 8)10)
33.65	1 : 3		f : 3		—		S II	10)
27.91	4 : 6		1 : 5		o : f		S II	2)10)
5199.50	f : 2		o : 2		—		S II	2)
94.08	4 : 8		1 : 4		f : 1		S II	2) 10)
84.07	5 : 7		1 : 5		2 : 8		S II	2)10)
82.57	6 : 8		2 : 5				S II	8)10)
80.19	1 : 3		o : 3		—		S II	10)
74.09	o : f		o : 1		—		S II	.
64.56	5 : 7		3 : 6		f : 2		S II	2) 8)10)
5054.85	6 : 10		2 : 7		f : 2		S II	2)10)
38.96	1 : 5		f : 5		—		S II	3)10)
11.00	2 : 4		o : 4		—		S II	2)10)
02.96	—		2 : f		—		A(?) —	.
4987.23	1 : 5		f : 5		—		S II	3)10)
79.95	4 : f		8 : 3		f : o		A I	1) 4) 7) 9)
59.51	3 : 6		1 : 6		o : f		S II	2)10)
45.77	3 : 7		2 : 5		o : f		S II	2)
42.21	1 : 3		f : 3		—		S II(?)	2)10)
30.82	6 : 10		3 : 9		o : 4		S II	2) 8)10)
28.97	6 : 10		3 : 9		o : 4		S II	2) 8)10)
26.76	f : 3		o : 3		—		S II	3)10)
21.39	4 : 7		4 : 6		o : f		S II	10)
21.20							—	.
4867.94	2 : 5		f : 5		f : 1		S II	2) 8)10)
66.85	3 : 6		2 : 5				S II	2) 8)10)
60.19	f : 1		1 : 2		—		S II(?)	.
48.99	5 : 8		2 : 6		o : 1		S II	3)10)
45.20	2 : 5		1 : 5		—		S II	3) 8)10)
38.82	2 : 4		1 : 4		—		S II	2)10)
18.56	f : 4		f : 2		—		S II	3)10)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
4816.90	6	12	3	10	2	8	S	II	2)10)
07.80	f	0	2	f	—		A	I	11?)
02.54	3	5	1	4	—		S	II	3?)10)
4798.42	f	0	1	f	—		A(?)	—	.
95.28	1	3	0	3	0	f	S	II	2)10)
91.99	1	2	0	2	—		S	II	10)
85.64	8	16	8	16	3	10	S	II	2)10)
80.52	4	1	8	3	1	0	A	I	1) 4) 6) 7) 9)
77.30	0	2	1	2	—		S	II(?)	2) 8)10)
76.61	2	6	2	5	0	f	S	II	2)10)
74.01	1	4	f	3	—		S	II	2)10)
67.28	4	7	3	5	f	3	S	II	2) 8)10)
66.27	4	7	3	5			S	II	3?)10)
53.05	f	2	0	1	—		S	II	10)
52.47	3	f	5	3	f	0	A	I	1) 4) 5) 7)9?)
44.53	1	4	f	3	—		S	II	3)10)
42.87	5	10	3	6	0	3	S	II	2) 8)10)
35.67	4	7	1	5	—		S	II	3) 8)10)
28.90	2	5	f	4	—		S	II	10)
28.49							S	II	3) 8)10)
20.56	6	12	4	8	f	4	S	—	8)10)
19.95							S	II	2)10)
05.00	10	20	5	13	5	15	S	II	2)10)
01.93	0	f	f	1	—		S	II	11)
4696.59	2	3	1	3	—		S	II	10)
93.48	5	7	3	5	f	1	S	II	2)10)
91.42	f	2	0	2	—		S	II	10)
78.89	7	13	5	12	1	6	S	II	2) 8)10)
73.56	f	2	0	2	—		S	II	10)
72.75	4	6	2	5	0	f	S	II	2)10)
66.42	f	1	f	2	—		S	II	10)
52.18	4	6	1	5	0	f	S	II	3?) 8)10)
44.17	f	0	3	1	—		A	—	8)10)
43.74					—				.
42.35	2	4	0	3	—		S	II	3)10)
29.66	1	2	f	3	—		S	II	3?)10)
22.99	5	8	3	8	f	1	S	II	2) 8)10)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
4614.86	2	f	5	2	f	o	A	I	1) 4) 7) 9?)
05.90	f	2	f	2	—		S	II	3) 8)10)
01.63	1	4	o	4	—		S	II	3)10)
4597.14	f	2	o	2	—		S	II	3?)10)
75.95	1	o	5	1	—		A	I	1) 4) 7) 9?)
58.21	f	2	o	1	—		S	II	2?)10)
43.12	2	5	2	8	f	4	S	II	2) 8) 10)
42.67	o	2	o	4			S	II	2?) 8) 10)
38.95	f	3	1	5	o	1	S	II	2)10)
30.21					—				
30.00	f	1	1	3	—		A&S	I&II	3)
29.78					—				10)
25.82	3	o	4	2	2	1	A	I	1) 4) 7) 9)
13.99	2	o	3	1	f	o	A	I	1) 4) 5) 7) 9?)
13.67									
08.29	o	2	f	2	—		S	II	2) 8) 10)
4490.68	1	o	2	1	f	o	A	I	1) 6) 7) 9?)
77.96	5	1	6	4	3	2	A	I	1) 4) 7) 9)
72.83	4	f	4	3	2	1	A	I	1) 4) 7) 9)
71.99	o	f	o	1	—		S(?)	—	10)
66.42	o	f	o	f	—		S(?)	—	11)
65.99					—			—	
60.92	o	1	o	2	—		S	—	
60.39					—			III(?)	3)10)
53.75	o	f	o	2	—		S	—	
41.94	4	1	4	3	2	1	A	I	1) 4) 7) 9)
31.13	o	1	o	3	—		S	II	3)10)
25.32	1	o	3	2	1	f	A	I	1) 7) 9)
23.22	f	o	1	o	—		A(?)	—	
12.66	1	o	1	f	—		A(?)	—	
07.80	f	3	1	5	—		S	II	3)10)
05.18	o	f	f	2	—		S	II	3)10)
4399.87	f	o	1	f	—		A	I	7)
96.55	1	4	o	6	—		S	II	3)10)
95.10	1	4	2	5	—		S	II	2)10)
91.76	1	o	3	1	—		A	I	6)
86.83	o	1	o	4	—		S	II	3)10)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
4372.20	0	1	0	4	—		S II	3)10)
* 69.71	1	0	1	0	—		A I	.
* 68.24	1	0	1	0	—		A I	.
65.76	8	10	5	10	1	5	S II	2) 8)10)
65.31	—		3	f	—		A I	1)
51 38	2	5	3	5	0	f	S II	10)
07.96	1	4	3	5	f	1	S II	3)10)
4297.27	1	4	3	5	0	1	S II	3^2)10)
91.54	5	8	4	8	1	4	S II	2) 8)10)
61.44	0	1	0	f	—		S —	3) 8)10)
60.74	0	1	1	3	—		S II	.
37.00	3	6	3	6	f	3	S II	2) 8)10)
30.10	1	4	1	5	0	1	S II	2)10)
24.00	6	10	5	12	1	5	S II	2) 8)10)
22.48	f	3	2	5	—		S II	10)
10.76	0	f	0	f	—		S(?) —	.
08.70	0	2	f	3	0	f	S II	2)10)
06.23	0	2	f	3	—		S II	10)
02.64	1	0	2	0	f	0	A I	.
01.46	0	3	0	3	—		S II	10)
4193.62	3	6	3	5	f	4	S II	8)10)
93.34	f	3	f	4			S II	2) 10)
79.76	4	8	4	10	1	8	S II	2) 8)10)
75.92	1	0	3	2	—		A I	1) 9^2)
60.14	0	3	1	6	—		S II	3^2)10)
57.54	0	3	f	3	—		S II	2)
* 57.30	1	0	1	0	—		A I	.
57.23	0	2	1	4	—		S II	2)10)
51.52	0	1	0	3	—		S II	2)10)
44.12	f	0	1	f	—		A I	1) 5)10^2)
40.37	2	6	3	8	0	2	S II	2) 8)10)
38.78	0	1	f	4	—		S II	3^2)10)
35.79	2	6	2	6	0	1	S II	2) 8)10)
18.81	1	4	1	4	1	2	S II	2)10)
17.69	1	4	1	4			S II	3^2) 8)10)
10.20	1	5	1	5	f	1	S II	2)10)
06.60	f	1	f	1	0	f	S II	2)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
4106.52	f : 1		f : 2		0 : f		S	II	2)10)
05.66	0 : 2		f : 1		—		S	II	2)10)
05.06			f : 2		—		S	II	10)
02.72	1 : 3		f : 3		0 : f		S	II	2)10)
4098.07	0 : 2		0 : 2		—		S	II	2)10)
96.22	1 : 2		f : 2		—		S	II	3?)10)
90.76	0 : 1		0 : 2		0 : f		S	II	2)10)
89.36	f : 2		f : 2		—		S	II	10)
* 77.68	2 : 1		2 : 1		—		A	I	.
75.70	2 : 6		1 : 6		f : 1		S	II	3)10)
72.30	1 : 3		f : 3		0 : f		S	II	2)
63.77	2 : 4		f : 4		1 : 2		S	II	2)10)
46.74	0 : 2		0 : 2		—		S	—	.
37.51	0 : 1		0 : 1		—		S	II	3)
* 36.70	2 : 1		2 : 1		—		A	I	.
36.61	1 : 3		1 : 4		0 : f		S	II	3)10)
* 24.48	1 : 0		1 : 0		—		A	I	.
24.19	3 : 6		1 : 6		2 : 3		S	II	3)10)
* 21.66	3 : 2		3 : 2		2 : 1		A	I	.
* 18.21	2 : 1		2 : 1		—		A	I	.
* 12.41	1 : 0		1 : 0		—		A	I	.
08.92	3 : 6		2 : 6		1 : 2		S	II	3)10)
07.44	0 : 1		f : 3		f : 1		S	II	3)10)
05.78	f : 2		1 : 3		f : 1		S	II	3)10)
01.58	f : 2		f : 4		0 : f		S	II	3)10)
3999.74	1 : 4		f : 3		—		S	II	3)10)
* 98.93	1 : 0		1 : 0		—		A	I	.
97.22	1 : 2		1 : 3		—		S	II	3)10)
94.01	0 : 1		0 : 3		—		S	II	3)10)
* 92.26	5 : 3		6 : 4		2 : 1		A	I	10)
* 87.70	2 : 1		2 : 1		—		A	I	.
86.70	4 : 8		4 : 10		2 : 3		S	II	2)10)
* 82.74	1 : 0		1 : 0		—		A	I	.
80.57	6 : 2		6 : 12		5 : 8		S	II	3)10)
80.18			0 : 3				S	II	3)10)
70.75	f : 2		1 : 3		—		S	II	3)10)
68.81	2 : 6		2 : 4		0 : f		S	II	3)10)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
3955.49	3 : 7		2 : 7		2 : 3		S	II	3)10)
50.74	2 : 5		1 : 7		2 : 3		S	II	3)10)
47.11	f : 3		0 : 3		f : 1		S	II	3)10)
46.80	0 : 3		0 : 3						3)10)
44.73	f : 2		0 : 2		—		S	—	10)
39.83	2 : 5		1 : 4		1 : 2		S	II	3)10)
38.80	f : 4		1 : 3		0 : f		S	II	3)10)
29.71	2 : 4		f : 4		1 : 2		S	II	3)10)
24.25	6 : 15		2 : 8		2 : 4		S	II	3)10)
23.50			2 : 5				S	II	3)10)
20.81	2 : 6		2 : 5		1 : 2		S	II	3)10)
19.68	1 : 5		2 : 4				S	II	3)10)
14.40	3 : 7		1 : 5		2 : 3		S	II	3)10)
01.39	1 : 3		1 : 4		0 : f		S	II	3)10)
3897.88	0 : 3		0 : 3		0 : f		S	III	2?)
91.78	2 : 5		f : 5		1 : 2		S	II	3)10)
71.39	2 : 5		1 : 4		0 : 1		S	II	3)10)
57.37	1 : 4		0 : 4		f : 1		S	II	3)10)
40.73	1 : 3		0 : 3		0 : f		S	II	3)10?)
34.85	2 : 5		1 : 4		0 : f		S	II	3)10)
* 28.74	2 · 1		2 : 1		—		A	I	.
* 15.81	5 : 2		5 : 3		1 : 0		A	I	.
11.54	f : 2		1 : 3		—		S	II	2?)
* 3794.18	3 : 1		3 : 2		—		A	I	.
72.69	f : 3		0 : 3		—		S	III	3)10)
70.41	0 : 2		0 : 2		—		S	II	3)10?)
53.78	f : 2		f : 3		—		S	II	3)10?)
40.65	1 : 4		1 : 4		f : 1		S	II	2)10)
37.82	0 : 2		0 : 3		0 : f		S	II	2?)10?)
25.54	f : 2		f : 3		—		S	II	2)10?)
14.45	f : 3		1 : 4		0 : f		S	II	3)10)
3699.60	f : 1		f : 2		—		S	II	3)10)
93.46	1 : 6		0 : 3		f : 1		S	III	2)11)
84.6	f : 1		f : 2		—		S	II	3)10)
81.6	f : 1		0 : 2		—		S	III	3)10)
79.3	0 : f		0 : 1		—		S	II	.
78.2	0 : f		f : 1		—		S	II	.

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
3659.4	3 : 10		1 : 6		1 : 2		S	III	2)10)
48.0	f : 1		0 : 2		—		S	II	2?)
33.6	f : 2		0 : 4		0 : 1		S	II	3)10)
24.7	0 : f		f : 1		—		S	II	.
23.9	0 : f		0 : 1		—		S		.
22.0	f : 1		f : 2		—		S	II	10)
20.9	f : 2		f : 3		0 : f		S	II	10)
19.4	0 : f		f : 1		—		S	II	10)
13.3	0 : f		f : 1		—		S	III	10?)
12.2	0 : 2		0 : 1		—		S	—	11)
08.9	0 : f		f : 1		—		S	II	.
06.6	2 : 3		f : 4		f : 1		S	II	3)10)
00.7	1 : 4		f : 3		1 : 2		S	II(?)	2)11)
3585.5	f : 1		0 : 2		f : 1		S	II	2?)10)
62.4	2 : 8		f : 6		1 : 4		S	III	2)11)
51.04	f : 4		0 : 2		f : 1		S	III	2)11)
40.2	1 : 5		0 : 3		f : 3		S	III	2)11)
28.9	0 : 2		0 : 1		0 : 1		S	III	2)11)
27.9	0 : f		0 : f		—		S	III	11)
26.1	0 : f		0 : f		—		S(?)	—	11)
25.4	—		0 : 1		—		S	II	2)10)
17.4	0 : 2		0 : 2		0 : 2		S	III	2)11)
06.5	0 : 2		0 : 2		0 : 1		S	III	2)11)
3495.1	—		0 : 1		—		S	II	3)10)
76.9	—		0 : 2		—		S	II	2)10)
66.7	—		0 : 1		—		S	II	3?)10?)
47.33	0 : 2		0 : 8		f : 3		S	III	2)11)
36.8	—		0 : 1		0 : f		S	II	3?)10)
28.9	—		0 : 1		0 : f		S	II	2)10)
23.78	0 : f		0 : 2		0 : f		S	II	10)
17.55	f : 5		f : 6		2 : 6		S	III	2)11)
14.5	0 : 1		0 : 4		f : 2		S	III	2)11)
09.8	—		0 : 1		—		S	II	3)10)
02.4	0 : 2		f : 4		f : 3		S	III	3)11)
3397.8	f : 3		f : 5		f : 3		S	III	2)11)
97.1							S	III	11)
85.5	—		0 : 2		f : 1		S	III	2)11)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
3366.1	—		0 : 1		—		S	II	2)10)
49.69	0 : 4		0 : 5		1 : 5		S	III	3?)11)
46.98	0 : f		0 : 2		f : 2		S	II	3?)10)
41.9	—		0 : 1		—		S	II	.
33.08	0 : 5		0 : 6		1 : 5		S	III	2)11)
20.97	0 : 2		f : 5		1 : 3		S	III	2)11)
01.2	0 : f		0 : 3		f : 2		S	III	11)
3289.2	—		0 : 1		—		S	II	10)
82.2	0 : 1		0 : 3		2 : 3		S	III	2)11)
70.0	0 : 1		0 : 3		f : 2		S	III(?)	3?)11)
69.0							S	II(?)	10)
08.4	—		0 : 1		—		S	II	3)10)
3199.7	0 : 1		0 : 6		f : 2		S	III	2)11)
67.5	0 : 1		0 : 4		f : 3		S	III	3)11)
3074.3	0 : 2		0 : 5		f : 5		S	III	3?)11)
53.0	—		0 : 1		—		S	II	3?)10)
28.91	0 : 1		0 : 3		0 : 1		S	II	2)10)
20.7	0 : 4		0 : 8		2 : 4		S	III	3)11)
16.4	f : 3		1 : 6		f : 2		S	II	2)10)
15.9							S	—	10)
11.4	0 : f		0 : 2		0 : f		S	II	3?)10)
2999.7	—		0 : 1		—		S	II	2)10)
94.0	0 : 1		0 : 3		1 : 3		S	III	3)11)
86.5	f : 3		0 : 6		2 : 3		S	II	2)10)
85.9							S	II	2)10)
83.7	—		0 : 1		—		S	III	10)
81.84	0 : f		0 : 4		0 : 1		S	II	3?)10)
73.46	—		0 : 1		—		S	II	2?)10)
72.2	1 : 7		1 : 5		3 : 5		S	II	2)10)
68.94	f : 3		f : 5		2 : 5		S	III	3?)11)
67.2	f : 2		1 : 5		f : 2		S	II	2)10)
61.1	—		0 : 4		0 : 2		S	III	3?)11)
54.0	—		0 : 3		—		S	II	.
44.3	—		0 : 1		f : 1		S	II	10)
36.2	—		0 : 4		1 : 2		S	III	3?)11)
26.87	f : 5		0 : 7		2 : 7		S	III	3?)11)
25.64	0 : f		0 : 2		0 : 1		S	II	10)

Table II, Bromine (continued)

Weve-lengths	Relative Intensities						Types	Remerks
	1		2		3			
	w	c	W	H	C+L	C		
2921.86		o : f		o : 2		o : 1	S II	3?)10)
17.19		o : 1		o : 4		f : 2	S II	2)10)
13.3		—		o : 1		—	S II	2)10)
10.7		—		o : 2		o : 1	S II	2)10)
05.8		o : f		o : 1		—	S II	2)10)
04.1		—		o : 1		—	S II	10)
00.1		o : f		1 : 3		1 : 3	S II	3?)10)
2893.39		f : 5		f : 6		3 : 4	S II	2)10)
92.9							S II	2)10)
92.0		—		o : 2		o : 1	S II	2)10)
87.1		o : f		o : 1		o : 1	S II	10)
75.37		o : f		o : 2		o : 1	S II	3?)10)
73.2		1 : 5		f : 6		1 : 3	S II	3?)10)
72.5							S II	3?)10)
66.97		o : 2		o : 3		f : 1	S II	3?)10)
46.1		o : f		f : 3		f : 1	S III	2)10)
14.0		—		o : 2		—	S II	3?)10)
07.5		—		o : 1		f : 2	S II(?)	2)10)
00.0		—		o : 2		—	S III	10)
2798.95		f : 5		1 : 5		2 : 3	S II	2)10)
70.5		—		o : 2		o : f	S II	3?)10)
66.65		o : f		o : 5		1 : 3	S III	3?)11)
46.4		f : 4		1 : 6		2 : 4	S II	.
46.0							S III(?)	.
28.4		o : f		o : 1		—	S II	3)10)
26.99		o : f		f : 3		1 : 2	S II	2)10)
25.2		—		o : 1		o : 1	S(?) II(?)	.
24.8								.
20.33		o : 2		f : 3		f : 1	S II	3?)
18.3		—		o : 1		1 : 1	S(?) —	10)
13.67		1 : 5		1 : 6		1 : 3	S II	3)10)
09.8		o : 1		f : 4		o : f	S II	10)
09.6								
2690.1		f : 2		f : 5		f : 2	S II	2)10)
89.9							S —	.
84.0		—		o : 1		f : 1	S II	10)
77.3		—		o : 3		o : 1	S III	11)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
2660.44	1 : 2		1 : 5		1 : 5		S	II	2)10)
58.6	—		0 : 4		0 : 2		S	III	11)
28.7	—		0 : 3		f : 2		S	--	.
26.44	0 : f		f : 5		f : 2		S	III	3)11)
13.1	0 : 1		0 : 6		1 : 4		S	III	3)11)
06.2	0 : f		0 : 4		0 : 2		S	III	3)11)
03.2	—		0 : 3		0 : 2		S	III	3)11)
01.8	f : 3		2 : 5		0 : 2		S	III	11)
01.17							S	II	3?)10)
2595.9	—		0 : 2		0 : 1		S	III	3?)11)
93.70	1 : 6		1 : 5		3 : 5		S	II	2)10)
89.1	0 : f		0 : 4		0 : 2		S	III	11)
86.9	—		0 : 1		—		S	II	2)10)
78.1	0 : 1		2 : 3		0 : 1		S	II	3)10)
77.8							S	II	10)
69.14	0 : f		1 : 2		0 : 1		S	II	10)
67.3	—		0 : 1		f : 1		S	II	2)10)
63.2	—		0 : 1		—		S	II	2)10)
56.9	1 : 5		2 : 7		4 : 10		S	II	2)10)
56.6							S	—	.
51.1	f : 1		f : 2		0 : 2		S	III(?)	11)
50.7							S	II(?)	3?)
41.42	1 : 5		2 : 8		3 : 8		S	II	2)10)
24.94	0 : 1		0 : 3		1 : 2		S	II	2)10)
21.69	1 : 7		2 : 8		4 : 10		S	II	2)10)
2499.3	0 : f		0 : 2		0 : 1		S	III	2)11)
98.4	—		0 : 1		—		S	II	2?)11)
95.18	0 : 1		f : 4		1 : 2		S	II	2?)11)
88.9	—		0 : 1		0 : 2		S	—	.
88.4							S	—	2)10)
2395.40	f : 3		1 : 8		1 : 5		S	II	2)10)
93.4	—		0 : 1		—		S	II	.
92.5	f : 4		2 : 10		2 : 6		S	II	10)
92.3									2)10)
89.74	2 : 10		3 : 9		3 : 8		S	II	2)10)

Table II, Bromine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
2388.98	f : 3		1 : 7		2 : 6		S	II	2) 10)
88.73									2) 10)
86.77	1 : 7		2 : 12		2 : 8		S	II	2) 10)
86.6									2) 10)
55.71	0 : 2		f : 5		f : 3		S	II	2) 10)
46.9	0 : 6		0 : 2		—		S	II	2) 10)
37.93	f : 3		1 : 4		2 : 5		S	II	2) 10)
36.96	0 : f		0 : 2		1 : 2		S	II	2) 10)
17.35	f : 2		1 : 4		1 : 4		S	II	2) 10)
13.8	—		0 : 1		0 : 1		S	II	10)
10.3	—		0 : 1		0 : 1		S	II	.
04.1	—		0 : 1		—		S	II	2)
2287.6	0 : f		0 : 2		f : 2		S	III(?)	2) 10)
85.2	—		0 : 1		f : 1		S	II	2) 10)
84.5	—		f : 1		0 : f		S	II	10)
81.4	—		f : 1		f : 1		S	II	2) 10)
80.6	—		0 : 1		—		S	II	2) 10)
70.4	—		0 : 1		f : 1		S	II	2)
45.9	—		0 : 1		—		S	II	.
43.0	—		0 : 1		—		S	II	.
37.0	—		f : 2		—		S	II	.

Notes:— 1) The first type of modes of broadening.
2) The second type of modes of broadening.
3) The third type of modes of broadening.
4) Lines disappeared when a capacity was put in the discharge circuit. (Goldstein).
5) Lines weakened by a capacity. (Galitzin and Willip).
6) Lines disappeared by a large capacity. (Galitzin and Willip).
7) Lines classified as arc type. (Kimura).
8) Lines regarded as spark type. (Kimura).
9) Lines classified as BrI. (L. and E. Bloch).
10) Lines classified as BrII. (L. and E. Bloch).
11) Lines classified as BrIII. (L. and E. Bloch).

Table III, Chlorine

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
6093.4	—		0 : 3		f : 4		S II	8)
5785.4	—		0 : f		0 : f		S II	.
5635.1	—		0 : 1		0 : 1		S II	8)
5570.4	—		0 : 1		0 : f		S II	.
5457.70	f : 3		f : 10		2 : 8		S II	6) 8)
57.28								2) 6) 8)
56.39								2) 6) 8)
45.12	1 : 4		f : 12		2 : 10		S II	6) 8)
44.41								2) 6) 8)
43.59								2) 6) 8)
23.70	2 : 6		f : 12		3 : 12		S II	6) 8)
23.44								2) 6) 8)
5392.30	2 : 4		1 : 9		2 : 8		S II	2) 8)
5285.8	0 : f		0 : 4		0 : 3		S II(?)	2) 8)
21.48	f : 4		f : 10		1 : 7		S II	2) 8)
18.07	2 : 7		1 : 12		2 : 10		S II	2) 8)
5193.6	—		0 : 1		0 : 1		S II	8)
89.74	0 : f		0 : 3		0 : 3		S II(?)	8)
76.0	0 : f		0 : 2		0 : 2		S II	8)
73.4	0 : f		0 : 2		0 : 3		S II(?)	8)
65.20	—		0 : 2		0 : 1		S II	8)
58.9	—		0 : 1		0 : f		S II	.
13.3	0 : f		0 : 4		0 : 2		S II	2) 8?)
03.18	f : 3		f : 8		f : 6		S II	2) 8)
5099.36	0 : 1		1 : 6		0 : 4		S II	2) 8)
78 36	2 : 5		1 : 10		1 : 7		S II	2) 8)
4995.7	0 : 1		0 : 5		f : 4		S II	2) 8)
70.3	0 : 1		0 : 5		0 : 3		S II	2) 8?)
43.1	—		0 : 2		0 : f		S II	.
24.90	0 : 1		f : 5		f : 3		S II	2) 8)
17.87	f : 3		1 : 10		f : 5		S II	2) 8)
04.91	1 : 5		1 : 10		1 : 8		S II	2) 8)
4896.91	1 : 6		1 : 10		2 : 10		S II	2) 8)
19.63	1 : 5		2 : 12		3 : 15		S II	2) 6) 8)
10.19	2 : 7		2 : 13		4 : 16		S II	2) 6) 8)
4794.67	3 : 8		2 : 13		5 : 18		S II	2) 6) 8)
85.41	0 : f		0 : 3		0 : 1		S II	2) 8)

Table III, Chlorine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
4781.49	0 : 3		1 : 8		1 : 5		S II	2) 8)
79.06	0 : f		0 : 3		0 : 2		S II	2) 8)
71.22	0 : f		0 : 4		0 : 2		S II	2)
68.80	0 : 1		1 : 5		0 : 4		S II	2) 8)
55.9	0 : f		0 : 2		1 : 0		S II	2) 8)
40.51	f : 2		1 : 5		f : 5		S II	2) 8)
* 4691.9	2 : 1		3 : 1		f : 0		A I	.
61.38	2 : 1		4 : 2		f : 0		A I	1) 4)
54.3	1 : 0		2 : 0		—		A I	.
24.23	1 : 0		2 : 1		—		A I	1) 5) 8)
01.19	4 : 2		6 : 4		2 : f		A I	1) 4) 5) 7?)8?)
4585.05	f : 1		0 : 1		0 : f		S II(?)	2) 8)
72.79	2 : 5		0 : 8		0 : 5		S II(?)	3) 8)
70.16	1 : 3		0 : 5		0 : 4		S II(?)	3) 8)
37.0	f : 1		0 : 2		0 : f		S II	2) 8)
26.44	6 : 3		8 : 5		5 : 4		A I	1) 4) 5) 7?)8?)
19.4	f : 1		0 : 2		0 : f		S II	2) 8)
04.50	f : 1		0 : 2		0 : f		S II	2) 8)
4497.45	0 : 1		0 : 2		0 : f		S II	2) 8)
91.25	1 : 0		3 : 1		f : 0		A I	1)
90.16	1 : 3		f : 5		0 : 3		S II	2) 8)
75.50	2 : f		5 : 4		2 : 1		A(?) I & II	5) 8)
69.57	1 : 0		3 : 1		f : 0		A I	1) 5)
46.35	0 : f		f : 1		—		S II	.
46.10	1 : f		1 : f		f : 0		A I	1)
38.74	2 : f		5 : 4		2 : 1		A I	1) 8)
03.61	2 : f		6 : 5		2 : f		A I	1) 5)
4399.37	f : 1		0 : 1		0 : f		S II	2) 8)
90.57	1 : f		3 : 2		5 : 3		A I	1) 4) 5)
89.95	3 : 1		6 : 5				A I	1) 4) 5) 7?)8?)
87.73	f : 0		2 : 1		f : 0		A I	1)
80.08	2 : f		4 : 3		1 : f		A I	1) 7?)8?)
73.12	2 : 5		1 : 8		f : 8		S II	2) 8)
71.72	f : 1		f : 1		f : 1		S(?) II(?)	.
69.68	1 : 0		4 : 2		1 : f		A I	1) 5) 9?)
63.48	2 : f		5 : 3		1 : f		A I	1) 5) 7)
43.82	4 : 8		5 : 10		f : 10		S II	2) 8)

Table III, Chlorine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
4336.37	1 : 3		f : 5		0 : 4		S II	2) 8)
33.13	0 : f		0 : f		—		S II	2) 8)
23.52	2 : f		5 : 4		2 : f		A I	1) 5) 7)
09.19	1 : 3		f : 7		0 : 5		S II	2) 8)
07.59	4 : 7		2 : 9		0 : 6		S II	2) 8)
04.21	1 : 3		f : 6		0 : 4		S II	2) 8)
4291.86	2 : 4		f : 7		0 : 5		S II	2) 8)
80.62	f : 0		f : 0		—		A(?) I(?)	1) 5)
76.63	f : 2		f : 5		0 : 3		S II	3) 8)
70.73	0 : 2		f : 4		0 : 3		S II	3) 8)
64.74	f : 0		1 : f		—		A I	1) 5)
61.35	f : 1		f : 3		0 : 2		S II	3) 8)
59.63	f : 2		f : 5		0 : 2		S II	2) 8)
53.53	2 : 7		1 : 10		0 : 10		S II	3) 6) 8)
41.44	2 : 6		1 : 10		0 : 9		S II	3) 6) 8)
35.61	0 : 2		f : 4		0 : 3		S II	3) 8)
34.14	f : 3		f : 8		0 : 4		S II	3) 6) 8)
26.58	f : 0		3 : 2		—		A I	1) 5)
25.14	0 : 1		f : 1		—		S II	3) 8)
09.87	f : 0		2 : 1		f : 0		A I	1) 5)
08.16	1 : 2		1 : 4		—		S II	2) 8)
4189.38	0 : f		0 : 1		—		S II	8)
58.02	0 : f		0 : 1		0 : f		S II(?)	2) 8)
47.20	0 : 1		f : 2		0 : f		S II	3) 8)
33.83	0 : f		0 : 1		—		S II(?)	8)
32.68	2 : 5		3 : 9		f : 5		S II	2) 8)
30.99	0 : f		0 : 1		—		S II(?)	8)
24.15	0 : 2		0 : 1		0 : f		S II	3) 8)
04.97	0 : 4		0 : 1		f : 1		S III	2)
4054.24	0 : 1		0 : 1		—		S II	8)
* 30.69	1 : 0		1 : f		—		A I	5)
3991.63	0 : 4		0 : 1		f : 2		S III	2) 9)
82.06	f : 3		f : 2		f : 1		S II	2) 5) 8)
61.77	f : 3		f : 2		1 : 2		S II	2) 8)
55.58	f : 4		0 : 3		f : 1		S II	2) 9)
17.72	f : 3		1 : 3		1 : 3		S II	3) 8)
16.83	1 : 4		1 : 4				S II	3) 8)

Table III, Chlorine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
3914.06	2 : 6		2 : 5		2 : 3		S	II	3) 8)
3884.05	0 : 3		f : 1		—		S	II	3) 8)
71.54	0 : f		f : 1		—		S	II	5)
68.84	1 : 5		1 : 3		0 · 1		S	II	3) 8)
61.01	3 : 12		2 : 8		4 : 6		S	II	3) 6) 8)
58.83	0 : 1		0 : f				S	—	.
55.74	0 : f		—		—		S(?)	—	8?)
54.00	f : 2		f : 2		0 : f		S	—	3) 5)
51.75							S	—	6) 8)
51.53	3 : 8		2 : 8		2 : 4		S	II	3) 6) 8)
51.17							S	II	3) 6) 8)
49.30	0 : f		0 : f		—		S(?)	—	.
45.83							S	II	3) 6) 8)
45.55	2 : 6		1 : 5		1 : 3		S	II	3) 6) 8)
43.39	1 : 4		2 : 3		f : 1		S	II	3) 8)
38.48	0 : 1		0 : 1		—		S	—	8)
33.50	2 : 4		2 : 3		1 : 3		S	II	3) 8)
30.96	0 : 1		0 : 1		—		S	—	3) 8)
29.55	0 : 2		0 : 2		0 : f		S	II	3) 8)
27.80	1 : 3		1 : 3		0 : 1		S	II	3) 8)
20.42	1 : 3		1 : 3		f : 2		S	II	3) 8)
18.58	f : 2		0 : 2		0 : f		S	II	8)
10.22	0 : 2		0 : 2		f : 1		S	II	3) 8)
09.70	f : 2		1 : 2				S	II	3) 8)
05.38	1 : 4		1 : 3		f : 2		S	II	3) 8)
3798.99	1 : 3		1 : 3		f : 2		S	II	8)
81.38	f : 3		2 : 3		0 : f		S	II	2) 8)
74.32	f : 2		0 : 2		0 : f		S	II	2) 8)
73.81	0 : 2		0 : 1				S	II	2) 8)
69.19	0 : 1		0 : 1		—		S	II	2) 8)
68.23	0 : f		f : 1		—		S(?)	II	2) 8)
67.65	f : 2		f : 2		0 : f		S	II	2) 8)
50.10	1 : 4		f : 3		f : 1		S	III	2) 8)
48.59	f : 3		0 : 1		f : 1		S	III	2) 8)
26.69	f : 0		f : 0		—		A(?)	—	.
25.91	f : 3		f : 3		0 : f		S	II	3) 8)
20.4	0 : f		0 : 1		—		S	III	9)

Table III, Chlorine (continued)

Wave-lengths	Relative Intensities						Types	Remarks
	1		2		3			
	w	c	W	H	C+L	C		
3689.1	f : 1		0 : 1		0 : f		S II	3) 8)
82.1	—		0 : 1		—		S III	9)
73.9	f : 1		0 : 2		f : 1		S II	2) 8)
68.1	0 : 1		0 : 1		0 : f		S II(?)	8)
59.91	0 : 1		0 : 1		0 : f		S II	2) 8)
58.50	0 : 1		0 : 2		0 : f		S III	2) 8)
50.24	f : 2		f : 2		0 : 1		S II	2) 8)
24.3	0 : 1		0 : 1		—		S III	3) 9)
13.9	—		0 : 1		—		S III	9)
02.2	—		0 : 2		—		S III	9)
3568.03	1 : 4		0 : 4		0 : 1		S —	3) 8)
09.09	0 : 2		0 : 2		0 : f		S II(?)	8)
3479.82	0 : 1		0 : 3		—		S II(?)	8)
3353.30	4 : 8		3 : 8		3 : 4		S II	2) 8)
40.36	0 : 4		0 : 4		1 : 6		S IV(?)	9)
29.06	4 : 12		1 : 10		2 : 5		S III(?)	2) 9?)
20.51	0 : 2		0 : 3		1 : 3		S III	2) 9)
16.78	0 : 2		0 : 2		—		S III	2) 8)
15.40	2 : 6		2 : 6		1 : 2		S II	2) 8)
13.18	0 : 1		0 : 1		—		S II	8)
07.86	1 : 3		0 : 3		0 : 1		S II	2) 8)
06.38	0 : 2		0 : 2		0 : f		S II	2) 8)
3289.72	0 : 2		0 : 2		f : 4		S III	9)
83.32	0 : 2		0 : 1		—		S III	2) 9)
76.72	f : 2		0 : 3		0 : 1		S II	2) 8)
59.24	f : 3		1 : 4		f : 4		S II(?)	2) 9)
51.03	0 : f		0 : f		—		S III(?)	9)
44.36	0 : f		0 : f		0 : 1		S III	2) 9)
02.96	f : 2		f : 4		0 : 1		S II	8)
3191.40	f : 8		0 : 5		f : 6		S III	2) 9)
39.28	0 : 3		0 : 2		0 : 3		S III	2) 9)
23.67	f : 2		f : 3		0 : 1		S II	8)
3071.58 71.31	f : 2		f : 3		f : 1		S II	2) 8)
63.38 63.07	0 : f		0 : 1		0 : 1		S III	9)
02.45	0 : f		0 : 1		0 : f		S III	9)

Table III, Chlorine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
2965.50		o : 1		o : 2		o : f	S	III	2) 9)
2783.14		o : f		o : f		o : 2	S	III	9)
82.43									9)
51.23		—		o : f		—	S	II(?)	9)
10.38		o : f		o : 1		2 : 4	S	III	9)
2691.49		o : 1		o : 1		f : 3	S	III	2) 9)
88.03		2 : 4		2 : 7		4 : 4	S	II	2) 8)
85.40		o : f		o : f		o : 2	S	III	2) 9)
84.75		o : 1		o : 1		o : 2	S	III	9)
82.40		—		o : 1		o : 1	S	III	9)
76.92		f : 2		1 : 6		2 : 3	S	II	2) 8)
69.57		o : f		o : 1		o : 1	S	III	9)
65.52		o : 2		o : 3		f : 5	S	III	2) 9)
63.20		—		o : 1		o : 1	S	III(?)	9)
61.56		o : 1		o : 2		f : 4	S	III	2) 9)
58.74		f : 3		1 : 5		2 : 3	S	II	2) 8)
51.16		—		o : 1		f : 2	S	III	9)
41.85		—		o : f		o : 2	S	III	9)
33.16		o : f		o : 1		o : 2	S	III	9)
32.68									9)
24.72		o : 2		o : 3		1 : 6	S	III	2) 9)
20.5		o : f		o : 2		o : 3	S	III	9)
20.08									2) 9)
18.76		o : f		o : 1		o : 1	S	III(?)	9)
16.99		o : 3		f : 5		1 : 7	S	III	2) 9)
11.45		o : f		o : 1		o : f	S	III	9)
09.50		o : 3		o : 4		f : 3	S	III	9)
03.50		o : 3		o : 4		o : 3	S	III	2) 9)
01.14		o : 1		o : 2		o : 2	S	III	9)
2595.17		—		o : f		o : f	S	III(?)	9)
88.80		—		o : f		o : f	S	III	9)
80.69		o : 2		o : 2		1 : 7	S	III	2)
80.41									
78.23		o : f		o : 1		f : 4	S	III	9)
77.13		o : f		o : 1		f : 4	S	III	2) 9)
65.29		f : 1		o : 1		f : 1	S	II	8)
64.87				o : 2					8)

Table III, Chlorine (continued)

Wave-lengths	Relative Intensities						Types		Remarks
	1		2		3				
	w	c	W	H	C+L	C			
2559.50	—		o : f		o : f		S	III	9)
47.00	o : f		o : 2		—		S	II	8)
32.46	o : f		o : 1		o : 3		S	III	9)
31.72	o : f		o : f		o : 1		S	III(?)	9)
28.04	o : 1		o : 1		o : 2		S	III(?)	9)
19.49	o : f		o : 1		f : 3		S	III	9)
05.71	—		o : f		o : f		S	III	9)
2484.25	—		o : f		o : f		S	III(?)	9)
15.49	o : f		o : f		—		S	III	9)
03.29	—		o : 1		—		S	III	9)
2370.37	o : f		o : f		o : 1		S	III	9)
40.64	—		o : f		—		S	III	9)
36.45	o : f		o : f		o : f		S	III	9)
23.50	o : f		o : 1		f : 3		S	III	9)
2251.50	f : 1		f : 2		2 : 3		S	II	8)
50.94	f : 1		f : 2		2 : 3		S	II	8)

Notes: — 1) The first type of modes of broadening.
2) The second type of modes of broadening.
3) The third type of modes of broadening.
4) Lines disappeared when a capacity was put in the discharge circuit. (Goldstein).
5) Lines disappeared from the "Grundspektrum". (Nelthorpe).
6) Lines recorded as Cl II. (Paschen).
7) Lines classified as Cl I. (L. and E. Bloch).
8) Lines classified as Cl II. (L. and E. Bloch).
9) Lines classified as Cl III. (L. and E. Bloch).

Plate I

Fig. 1, $SnCl_4$, Tube I

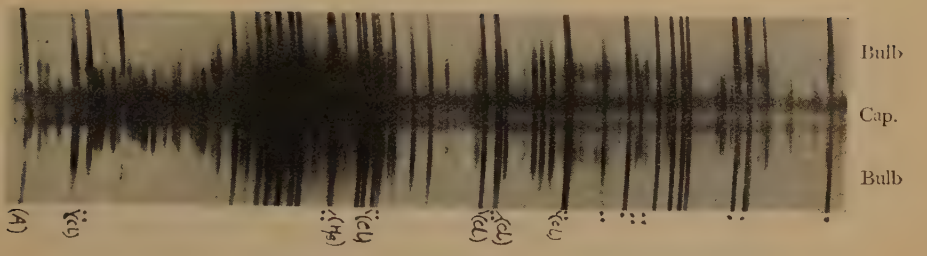


Fig. 2, Sn–Spark

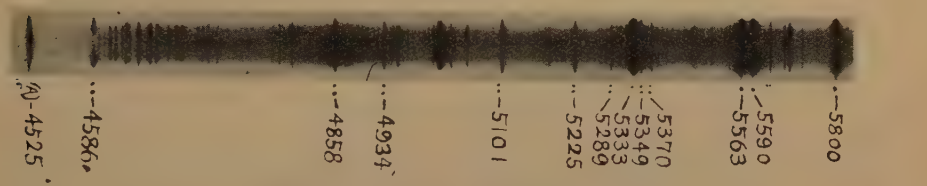


Fig. 3, Chlorine, Tube I

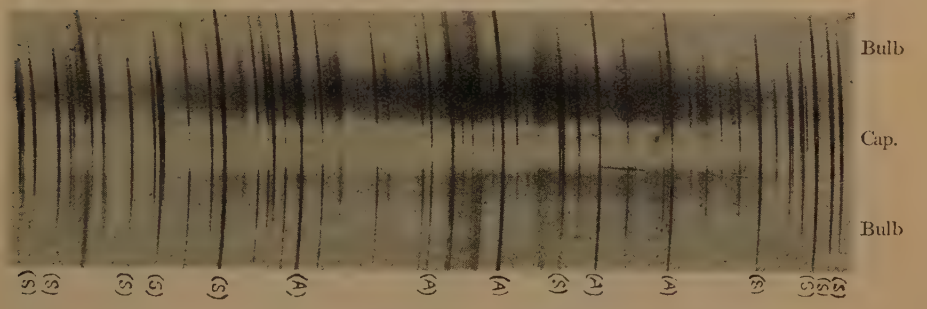


Fig. 4, Chlorine, Tube II

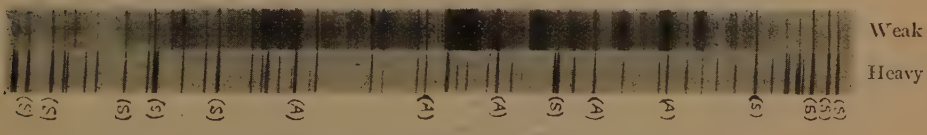


Fig. 5, Chlorine, Spark

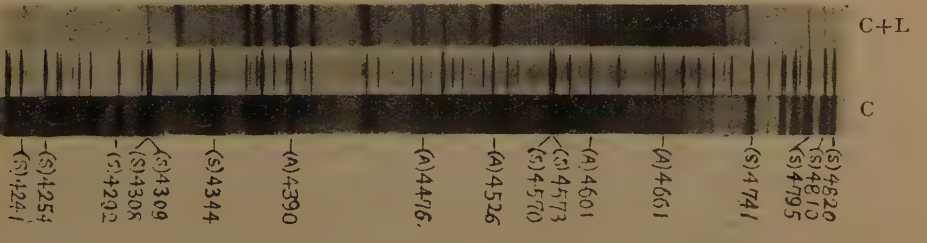


Plate II

Fig. 6. Sb-Spark

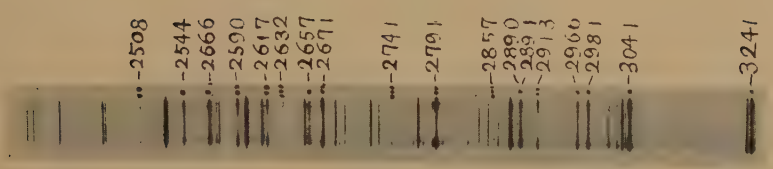


Fig. 7, $SbCl_5$ H-Variation

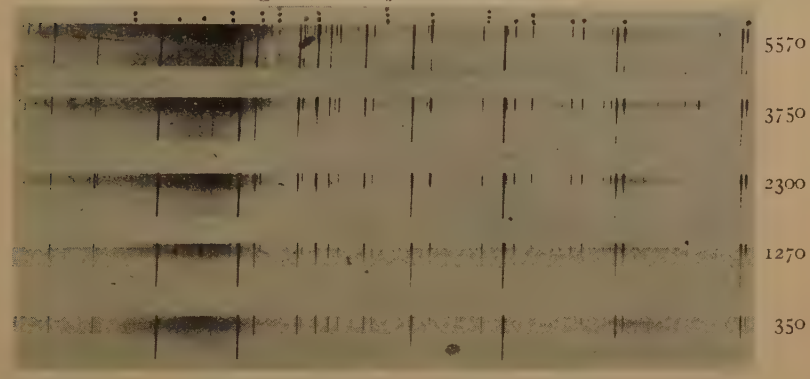


Fig. 8, $SbCl_5$, C-Variation

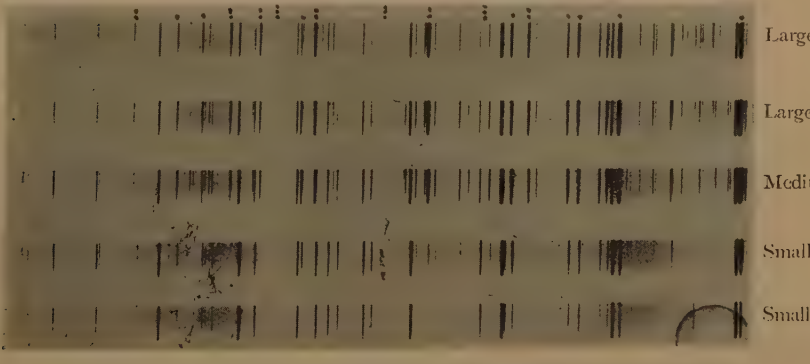


Fig. 9, $SbCl_5$, L-Variation

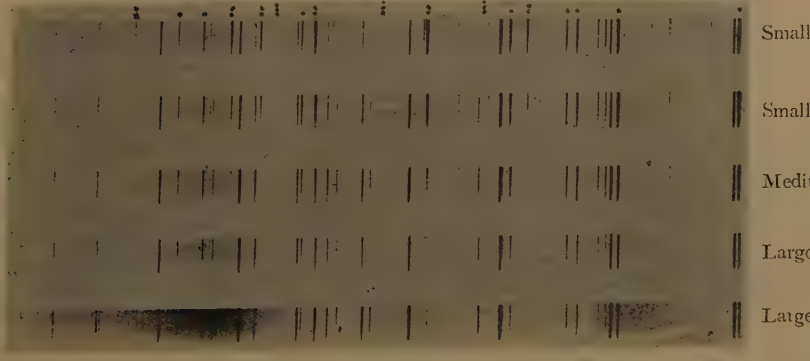


Plate III

Fig. 10, Iodine, H-Variation

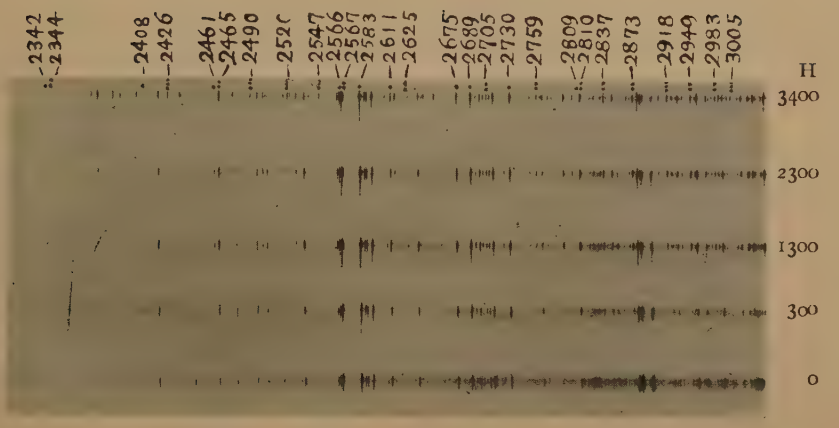


Fig. 11, Iodine, C-Variation

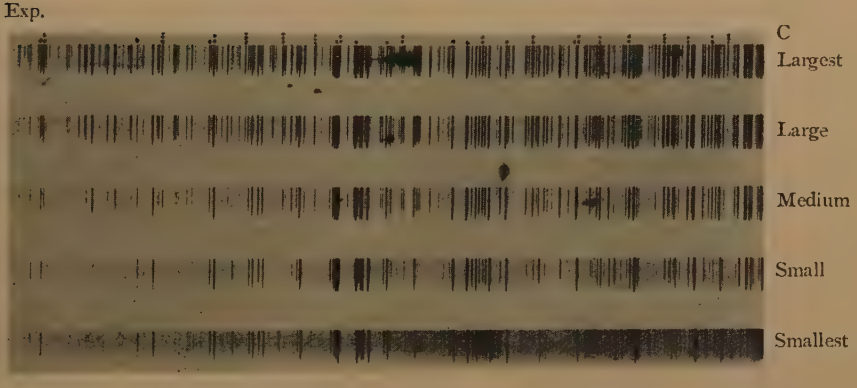
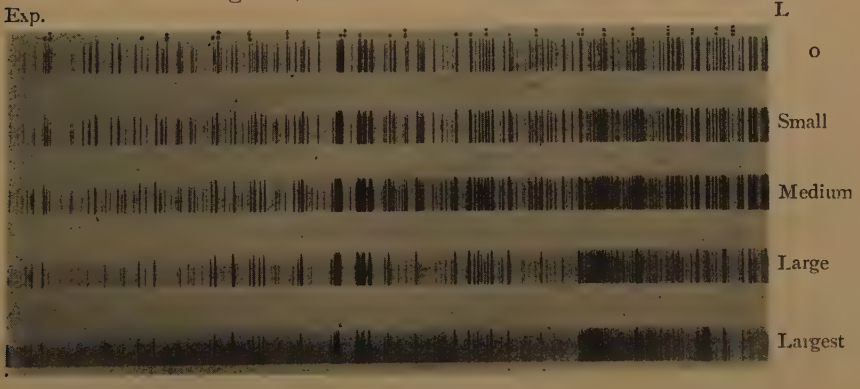


Fig. 12, Iodine, L-Variation



On the Electrolytic Reduction of Ketones. Part I. Reduction of α, β-Unsaturated Ketones

By

Goro Shima

(Received October 12, 1929)

The carbonyl group in α,β-unsaturated ketones is, in general, reducible to the secondary alcoholic group only with great difficulty, so that, when such ketones are subjected to reduction the corresponding saturated ketones are produced in most cases, but not saturated alcohols[1] which are obtained only very rarely. Sometimes condensation of two molecules is brought about by the addition of hydrogen to the unsaturated bond as was observed by Harries[2] and his co-workers, thus—

$$2C_6H_5\cdot CH=CH\cdot CO\cdot CH_3 + 2H = \begin{matrix} C_6H_5\cdot CH\cdot CH_2\cdot CO\cdot CH_3 \\ | \\ C_6H_5\cdot CH\cdot CH_2\ CO\cdot CH_3 \end{matrix}$$

$$2C_6H_5\cdot CH=CH\cdot CO\ C_6H_5 + 2H = \begin{matrix} C_6H_5\cdot CH\cdot CH_2\cdot CO\cdot C_6H_5 \\ | \\ C_6H_5\cdot CH\cdot CH_2\cdot CO\cdot C_6H_5 \end{matrix}$$

As previously reported[3] I succeeded in reducing cinnamic aldehyde electrochemically to the corresponding saturated alcohol with a yield of more than 70%. An attempt was now made to extend the study to the unsaturated ketones such as benzalacetone and benzalacetophenone, which, however, could not be reduced to the saturated alcohols, the main reduction product being the saturated ketone, as in the case

1. Wallach, Ann., **275**, 111 (1893); Ann., **359**, 283 (1908); Kerp, Ann., **290**, 148 (1896)
2. Ber., **29**, 380 (1896); Ann., **296**, 295 (1897)
3. These Memoirs, **12**, 69 (1928)

of purely chemical reduction. Engler and Leist[1] once reported that they had obtained phenylbutyl alcohol by reducing an alcoholic solution of benzalacetone with sodium amalgam, but this was disproved by Harries and Eschenbach[2] who could isolate only benzyl acetone and dibenzyl diacetone as the reduction product.

There is a short report on the electrolytic reduction of benzalacetone by Law[3], who electrolysed in a neutral cathode solution consisting of ethyl acetate, alcohol, water and potassium acetate with a lead or copper cathode and obtained benzyl acetone and dibenzyl diacetone.

When I electrolysed benzalacetone in an alcoholic caustic soda solution with a mercury cathode, a large quantity of a resinous substance was produced together with some benzyl acetone and dibenzyl diacetone, and beside these a new substance hitherto not described in chemical literature was obtained. It was a yellowish substance boiling at 195°–196° under 3 mm. pressure and combining with bromine at ordinary temperatures, and showing the existence of two double bonds when tested by Hanus' method. As a result of molecular weight determination and elementary analysis it was confirmed to be a pinacone having the composition,

$$\begin{array}{l} C_6H_5{\cdot}CH{=}CH{\cdot}C(OH){\cdot}CH_3 \\ \qquad\qquad\quad | \\ C_6H_5{\cdot}CH{=}CH{\cdot}C(OH){\cdot}CH_3 \end{array}$$

When an alcoholic sodium bicarbonate solution was employed as the the cathode solution, formation of the resinous substance and the pinacone greatly decreased, while the yield of benzyl acetone was increased to more than 90%. On the other hand the use of a cathode other than mercury, such as lead or copper, was found to favour the formation of dibenzyl diacetone and pinacone.

The reduction of benzalacetophenone was carried out by Schneidewind[4] and by Harries and Hübner.[5] The latter authors obtained benzyl acetophenone and dibenzyl diacetophenone by reducing a glacial acetic acid solution with zinc, and diphenyl propyl alcohol and a dihydric

1. Ber., **6**, 255 (1873)
2. Ber., **29**, 380 (1896)
3. J. Chem. Soc., **101**, 1016 (1912)
4. Ber., **21**, 1325 (1888)
5. Ann., **296**, 295 (1897)

alcohol of the cyclohexane series on working with an acidified alcoholic solution and sodium amalgam. The electrolytic reduction of benzalacetophenone was first undertaken by Kiyoshi Yamasaki[1] who electrolysed an alcoholic solution acidified with a few drops of sulphuric acid, using lead or copper as the cathode, and isolated the unsaturated pinacone,

$$\begin{array}{l} C_6H_5\cdot CH=CH\cdot C(OH)\cdot C_6H_5 \\ \qquad\qquad\qquad\quad | \\ C_6H_5\cdot CH=CH\cdot C(OH)\cdot C_6H_5 \end{array}$$

On electrolyzing benzalacetophenone in an alcoholic sodium bicarbonate solution to which some ether had been added, at 35°–40°C using mercury as the cathode, I obtained besides benzyl acetophenone and dibenzyl diacetophenone, a substance very much resembling the pinacone found by Yamasaki, but having the melting point about 10° higher. All attempts to change this pinacone as well as dibenzyl diacetophenone to the dihydric alcohol of the cyclohexane series above mentioned by further reduction having been unsuccessful, I repeated the reduction of benzalacetophenone according to the Harries and Hübner method, but could obtain only the unsaturated pinacone melting at 194°–195°, not the one that the German authors claim to have isolated.

When the reduction of benzalacetophenone was conducted at a lower temperature, that is, at about 20°–25° addition of hydrogen to the double bond chiefly took place, and benzyl acetophenone was produced with a 70%—75% yield.

The influence exerted by ether on the reduction is rather remarkable. The reduction conducted with an alcoholic solution containing no ether yielded, for the most part, a resinous substance and the reduction-products before mentioned only in very small quantities. The bad effect of alcohol on the reduction of aldehyde[2] was also observed in the above reduction, in which the formation of benzyl acetone and benzyl acetophenone decreased when the concentration of alcohol was increased.

Inferring from the above confirmed fact that an unsaturated pinacone is produced by the reduction of α, β-unsaturated ketone, the view expressed by Law[3] concerning the formation of desoxymesityl oxide

1. Dissertation not yet published
2. These Memoirs, **11**, 426 (1928); **12**, 71 (1929)
3. J. chem. Soc., **101**, 1016 (1912)

from mesityl oxide may be regarded as very probable. Harries and Hübner[1] assumed the intermediate formation of a diketone (I) which was thought by them to change into desoxymesityl oxide by dehydration, thus—

$$2\ Me_2C{=}CH\,COMe + 2H = \begin{matrix} Me_2C{\cdot}CH_2{\cdot}COMe \\ | \\ Me_2C{\cdot}CH_2{\cdot}COMe \end{matrix} \quad (I)$$

$$= Me_2C\begin{matrix} CH_2-C{\cdot}Me \\ \diagup\!\!\diagdown \\ CMe_2{\cdot}C{\cdot}COMe \end{matrix} + H_2O$$

The behaviour of desoxymesityl oxide in changing to tetramethyl succinic acid by oxidation and in forming an oxime, $C_{12}H_{21}{=}NOH,H_2O$ was taken by them to support their view. It was, however, made clear by Law's experiment that the substance which gave tetramethyl succinic acid by oxidation, and changed into an oxime on acting upon hydroxylamine was not desoxymesityl oxide but the intermediate diketone (I). It was further found by him that the reduction of mesityl oxide in an alkaline solution took place in two different ways and gave rise to the unsaturated pinacone of the formula $\begin{matrix} Me_2C{=}CH{\cdot}C(OH)Me \\ | \\ Me_2C{=}CH{\cdot}C(OH)Me \end{matrix}$ together with the diketone (I), and this pinacone changed into desoxymesityl oxide as the result of the rearrangement. Though in this experiment Law did not succeed in isolating the unsaturated pinacone in the pure state, its existence becomes now quite certain, judging from the result of this work, in which isolation of the unsaturated pinacone was effected.

Experimental

In the following experiments a porous cell was used as the cathode compartment and the cathode solution was always agitated while being electrolysed.

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1. loc. cit.

A. Electrolytic Reduction of Benzalacetone

1. Caustic soda solution.

Cathode solution : 100 c.c. alcohol + 10 c.c. 15% NaOH
+ 10 gms benzalacetone.
Cathode : Mercury (50 sq. cm.). Temp : 30°–40.°
Anode solution : 10% NaOH. Current : 2 amp.
Current quantity : 5 amp.-hour.

After electrolysis, the cathode solution, coloured deep red, was diluted with water, and neutralized with dil. H_2SO_4, when a brown resinous substance separated out This was repeatedly treated with ether, and from the ether extract, the ether was evaporated after dehydration. The oily residue, coloured dark red, was subjected to fractional distillation under reduced pressure, and the following fractions were obtained :—

A part boiling at 100°–110° under 5 mm. pressure	30–35%
„ „ „ „ 210°–220° „ „ „	25–30%
Residue	35–40%

The first fraction is a colourless resinous oil boiling at 234°–235° under ordinary pressure, and having a density of 0.9892. The result of analysis showed it to be benzyl acetone as follows :

0.2051 gm. substance : 0.6117 gm. CO_2 and 0.1496 gm. H_2O,
C=81.32% (Calc. 81.02%), H=8.16% (Calc. 8.17%).

By treating its alcoholic solution with p-nitrophenyl hydrazine hydrochloride, its nitrophenyl hydrazone was obtained as beautiful orange coloured needles melting at 113°–114°.

The second fraction distilled at 210°–220° under 5 mm. pressure was found to crystallize partly. By treating it with petroleum ether to dissolve oily matter, a white crystalline substance with the melting point of 161° was isolated. This was proved to be dibenzyl diacetone as a result of the following analysis :

0.1316 gm. substance : 0.3904 gm. CO_2 and 0.0593 gm. H_2O,
C=80.91% (Calc. 81.63%), H=7.03% (Calc. 7.48%).

By the action of phenylhydrazine it easily changed into a hydrazone which, when heated, became brown at 170° and melted at 194°.

From the portion soluble in petroleum ether a pale yellowish resinous substance boiling at 194°–195° under 3 mm. pressure was isolated. Its density was found to be 1.0842 (20°). The results of analysis were as follows:

0.1833 gm. substance: 0,5492 gm. CO_2 and 0.1184 gm. H_2O,

C=81.72% (Calc. 81.63%), H=7.22% (Calc. 7.48%).

The molecular weight was determined by the ebullioscopic method benzene being used as the solvent, and the values 308.9 and 302.3 were obtained for the calculated value, 294.

In order to find out the number of double bonds, 0.1436 gm. of the substance was dissolved in 10 c.c. of chloroform and treated with 25 c.c. of an iodine solution. After this had been allowed to stand for 2 hours, with occasional shaking, 10 c.c. of 10% potassium iodide solution was added, and the whole was titrated with a sodium thiosulphate solution, 1 c.c. of which corresponded to 0.0120 gm. of iodine. The volume of the thiosulphate solution found was 65.3 c.c. as opposed to 85.1 c.c. which was the value found in the blanc test.

$$\text{Iodine value} = \frac{(85.1-65.3)\times 0.0120\times 100}{0.1436} = 165.5$$

$$\text{No. of double bond} = \frac{165.5\times 294}{126.9\times 2\times 100} = 1.92$$

From the results of the above experiments the substance may be concluded to be diphenyl dimethyl dioxyhexadiene of the formula,

$$\begin{array}{l} C_6H_5\cdot CH=CH\cdot C(OH)\cdot CH_3 \\ \qquad\qquad\qquad\quad | \\ C_6H_5\cdot CH=CH\cdot C(OH)\cdot CH_3 \end{array}$$

When copper was used as the cathode in place of mercury the yield of benzyl acetone decreased from 35% to 16%, while that of the unsaturated pinacone and of dibenzyl diacetone increased from 18% to 35% and from 7% to 20% respectively.

2. Sodium bicarbonate solution.

In order to ascertain the conditions essential for obtaining benzyl acetone, the influences of cathode material, of temperature, of current density and of concentration of alcohol on the electrolysis of benzal-

acetone were studied, an alcoholic sodium bicarbonate solution being used as the cathode solution. The cathode solution after electrolysis was treated in the same way as the caustic soda solution previously described.

(a) Influence of cathode material

Cathode solution : 50 c.c. alcohol + 10 c.c. water + 10 gms. $NaHCO_3$ + 5 gms. benzalacetone.

Temperature : 20°–25°; Current density : 2 amp.

Current quantity : 4 amp. hour.

The yield of the reduction-products was as is given in the following table.

Cathode	Benzalacetone %	Pinacone %	Dibenzyldiacetone %
Hg	78	12	3
Pb	66	15	8
Cu	30	37	24

(b) Influence of temperature

Cathode solution : 40 c.c. alcohol + 20 c.c. water + 10 gms. $NaHCO_3$ + 5 gms. benzalacetone.

Cathode : Hg.

Other condition were maintained the same as before. The yields were found to be as follows :

Temp.	Benzylacetone %	Pinacone %	Dibenzyldiacetone %
10°–15°	72	15	6
20°–25°	84	10	2
35°–40°	90	–	–
45°–55°	84	–	–

(c) Influence of current density

Cathode solution : 30 c.c. alcohol + 30 c.c. water + 10 gms. $NaHCO_3$ + 5 gms. benzalacetone.

Temp. : 20°–25°.

The yield of the reduction products was as follows:

Current density amp./100 sq.cm.	Benzylacetone %	Pinacone %	Dibenzyldiacetone %
2	87	6	–
4	86	8	3
6	90	–	–
8	91	–	–

(d) Influence of concentration of alcohol

All the conditions were the same as in (a). The yields of the reduction products were:—

Cathode solution		Benzylacetone %	Pinacone %	Dibenzyldiacetone %
Alcohol (c.c.)	Water (c.c.)			
60	—	72	20	4
50	10	78	12	3
40	20	84	8	2
30	30	86	8	2
20	40	89	–	–

With less alcohol, as the solubility of benzalacetone in the cathode solution becomes insufficient, current effiiciency is greatly lowered.

From the above results, the conditions necessary for obtaining the best yield of benzyl acetone may be summarized as follows:

Cathode: Mercury. Anode: Platinum or lead.

Cathode solution: 40–50% alcohol containing an excess of $NaHCO_3$.

Anode solution: 5% NaOH solution. Temp.: 30°–35°.

Current density: 6–8 amp./100 sq. cm.

It is better to add the benzalacetone to the cathode solution little by little in the course of electrolysis, and to keep the cathode solution always agitated, constantly conducting a current of carbon dioxide into it.

B. Electrolytic Reduction of Benzalacetophenone

For the electrolysis a cathode solution consisting of 100 c.c. of alcohol and 30 c.c. of ether, in which 10 grams of sodium bicarbonate

and the same amount of benzalacetophenone were dissolved, was taken. This was electrolysed with the cathode of mercury by passing a current of 2.5 amperes. A platinum plate dipped in 10% caustic soda solution was used as the anode. In the course of electrolysis a white precipitate gradually accumulated in the cathode chamber and finally made the cathode solution muddy. After 8 ampere-hours of electricity had been passed, the cathode solution was diluted with water and treated with ether several times so as to dissolve soluble products. By this treatment a white substance was obtained suspended in the ethereal layer.

When collected its amount was found to correspond to 35%–45% of the original substance. After dehydration the ether was next evaporated from the ethereal solution, and a residue consisting of a resinous substance and a white crystalline substance was obtained. It was now treated with alcohol, and from the portion insoluble in alcohol a white crystalline substance melting at 194°–195° was isolated with a yield of 25%–30%. From the part soluble in alcohol a substance boiling at 210°–215° under 20 mm. pressure and crystallizing at once was collected with 10%–15% yield, together with a dark brown substance, the quantity of which was found to correspond to 25%–30%.

The substance distilled at 210°–215° under 20 mm. pressure was purified by crystallizing it from alcohol, and a colourless substance crystallizing in large plates with the melting point of 73° was obtained. It was analysed with the following results:

0.1778 gm. substance: 0.5560 gm. CO_2 and 0.1055 gm. H_2O,
C = 85.39%, H = 6.60%.
Calc. for $C_{15}H_{14}O$, C = 85.69%, H = 6.72%.

It could quantitatively be transformed into nitrophenyl hydrazone melting at 137°–139°, when treated with p-nitrophenyl hydrazine hydrochloride. Thus the substance was confirmed to be benzyl acetophenone.

The second substance crystallizing in white fine needles and melting at 194°–195° was found to dissolve in ether, benzene, toluol and xylol but with difficulty in alcohol. It gave the following results when analysed:

0.1885 gm. substance: 0.5933 gm. CO_2 and 0.1081 gm. H_2O,
C = 85.82%, H = 6.41%.
Calc. for $C_{30}H_{22}O_2$, C = 86.10%, H = 6.26%.

Its molecular weight was found ebullioscopically to be 413 or 433 by using benzene as the solvent, while the calculated value is 418.

The number of double bonds was also determined by Hanus' method following the manner previously described, and the value 1.92 was obtained. There remains, therefore no doubt that the substance is 1,3,4,6-tetraphenyl-3,4-oxy-hexadiene having the composition,

$$\begin{array}{l} C_6H_5\cdot CH=CH\cdot C(OH)\cdot C_6H_5 \\ \quad\quad\quad\

Cathode solution			Temp.	Benzyl acetophenone %	Unsaturated pinacone %	Dibenzyl diacetophenone %	Resinous matter %
Alcohol	Ether	Water					
100 c.c.	—c.c.	—c.c.	20°–25°	—	4	2	80
〃	—	30	35°–45°	12	35	45	7
80	20	—	50°–55°	20	14	28	18
〃	〃	30	35°–40°	24	14	20	20
〃	〃	〃	15°–20°	68	8	1	20
70	30	〃	〃	70	–	–	20

In conclusion, the writer wishes to express his heartiest thanks to Professor M. Matsui for his kind guidance and encouragement throughout this investigation.

Electrolytic Reduction of Nitriles. Part I

By

Kōichiro Ogura

(Received October 18, 1929)

The electrolytic reduction of nitriles was once undertaken by Felix B. Ahrens[1], who succeeded in isolating the corresponding primary amines but only with a very poor yield. To investigate the problem much more fully it was attempted to reduce benzonitrile, tolunitrile and benzylcyanide electrolytically under various conditions and to seek the best method by which they could be transformed into the corresponding amines.

Generally speaking, as nitriles are reducible only with great difficulty, their hydrolysis sometimes takes place far more easily than their reduction, and this makes the current efficiency for forming amines very low. Such a property predominates more in aliphatic nitriles than in the aromatic, so that benzylcyanide can hardly be reduced in an alkaline solution, unless the alkali is kept exceedingly dilute. An alcoholic solution consisting of 40 c.c. of 15% ammonium sulphate solution and 40 c.c. of 95% alcohol, when made slightly alkaline by the addition of 3 c.c. of 6N-ammonia, was found to give comparatively better results. An acid solution neither concentrated nor in a dilute state gave good results. The aromatic nitriles such as benzonitrile and tolunitrile, however, are reduced with more ease both in an alkaline and in an acid solution, though in 10% caustic soda solution they undergo hydrolysis partly.

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1 Zeit. Elektrochem., **3**, 99 (1896)

Experimental

1 Reduction of benzonitrile

About 3 grams of benzonitrile were added to the cathode solution consisting of 40 c.c. of 10% sulphuric acid and 40 c.c. of 95% alcohol. The solution was electrolysed in a porous cell with a lead cathode of about 30 sq. cm, which was carefully prepared by changing its surface first into the peroxide and then into the metallic form of spongy structure. The temperature of the bath was maintained at 25°-30° C. After passing a current of 0 45 amperes (current density, 0.015) for 14 hours the cathode solution was nearly neutralized with caustic soda, filtered and evaporated in a water bath to drive off alcohol. It was then made strongly alkaline by adding caustic soda and treated with ether so as to extract benzylamine. When the ether was evaporated from the ether extract after dehydration, a yellowish oil boiling at 183° C. was isolated. It had a strongly alkaline reaction and changed into the carbonate on absorbing carbon dioxide from the air, so that its isolation from the cathode solution must be conducted as promptly as possible, otherwise the amine changes into the carbonate having a white crystalline form and melting at 114°. It was confirmed to be benzylamine by transforming it into its hydrochloride and platinum double salt on the one hand, and by analysing it on the other. The nitrogen content was determined by Kjeldahl's method as follows:

0.2216 gm. substance gave 0.0217 gm. nitrogen

N = 9.82% (calc. 9.75%)

The electrolysis was also conducted with an alkaline solution consisting of 3 grams of benzonitrile in 40 c c. of 10% caustic soda solution mixed with 40 c.c. of 95% alcohol. When electrolysis was over the cathode solution was made slightly acidic by adding dilute sulphuric acid, filtered and evaporated in a water bath. Now caustic soda was added to make it strongly alkaline and repeatedly extracted with ether, which was found to have dissolved benzamide besides benzylamine. After being dehydrated with anhydrous sodium sulphate, the ether extract was treated with dry hydrochloric acid gas, when the amine separated out as the hydrochloride. The hydrochloride was filtered, and from the etherial filtrate benzamide was isolated as a white crystalline substance melting at 127°. It was analysed by Kjeldahl's method with the following result:

0.2170 gm. substance gave 0.0245 gm. nitrogen

N = 11.30% (calc. for benzamide, 11.57%)

The alkaline solution from which benzylamine and benzamide were extracted with ether was also found to contain some benzoic acid. The acid was isolated from the solution by acidifying it with dilute hydrochloric acid, and examined closely.

On the assumption that hydrolysis of the nitrile would be greatly suppressed by the use of a neutral electrolyte, to the cathode solution, prepared by dissolving 3 grams of benzonitrile in 40 c c. of alcohol was added 40 c.c. of 15% ammonium sulphate solution and it was then electrolysed by passing a current of 0.017 amp/cm^2 for 14 hours at 27°–31°. As is shown in the following table, the yield of benzylamine was greater than that obtained in electrolysis either of an acid or of an alkaline solution.

Electrolyte	Yield of benzylamine, %
15% $(NH_4)_2SO_4$	49.50
10% H_2SO_4	27.49
5% H_2SO_4	24.03
10% NaOH	30.73
5% NaOH	27.00

2 *Reduction of benzylcyanide*

Electrolytic reduction of benzylcyanide was undertaken just in an analogous manner to the case of benzonitrile. From a sulphuric acid solution only a very small quantity of the corresponding amine was obtained as its hydrochloride, melting at 213°. From a dilute alkaline solution, however, none at all was produced, and phenylacetamide melting at 152°–153° and phenylacetic acid were obtained instead of it. Phenylacetamide was confirmed by analysis and also from its property of changing into phenylacetic acid on hydrolysis.

0.2103 gm. substance gave 0.0213 gm. nitrogen

N = 10.15% (calc. 10.37%)

Phenylacetic acid was volumetrically confirmed by titrating it with $\frac{1}{10}$N–NaOH solution.

By using a neutral solution containing ammonium sulphate phenylethylamine was produced with a yield of 13%. It was found to boil at 198° and to be so strongly alkaline as to change into the carbonate in air. Its hydrochloride melting at 216° was analysed by Kjeldahl's method.

0.1298 gm. hydrochloride gave 0.0117 gm. nitrogen

N = 8.61% (calc. 8.91%)

The yield of phenylethylamine obtained by electrolysing a solution containing 3 grams of nitrile, 40 c.c. of alcohol and also 40 c.c. of the solution described in the following table, with a current of 0.015 ampere/cm^2 for 14 hours is here given :—

Electrolyte	Phenylethylamine, %
10% $(NH_4)_2SO_4$	13.05
10% H_2SO_4	2.40
5% H_2SO_4	2.11
15% HCl	1.90
10% NaOH	0.

Lead amalgam, zinc amalgam, mercury and platinum were also used as the cathode, but none of them surpassed lead in reduction efficiency.

3 *Reduction of paratolunitrile*

The cathodic behaviour of paratolunitrile was very much like that of benzonitrile previously described. The best result was obtained by using a 10–15% ammonium sulphate solution containing about 3 c.c. of 6N-ammonia as the cathode solution. Nearly 57% of the nitrile was changed into p-tolubenzylamine when electrolysis was continued for 14 hours with a current of 0.0175 amp/cm^2 at 30°. p-Tolubenzylamine was obtained as a colourless liquid boiling at 193° and having a strongly alkaline reaction. It absorbed carbon dioxide from the air and changed into the carbonate melting at 116°. Its hydrochloride melting at 232° was analysed.

0.2735 gm. hydrochloride gave 0.0226 gm. nitrogen

N = 8.26% (calc. 8.91%)

In a 10% sulphuric acid solution reduction of p-tolunitrile took place only in a very small degree, but was not accompanied by hydrolysis, while in a 10% caustic soda solution the reduction and hydrolysis took place side by side and produced p-toluamide together with p-tolubenzylamine. p-Toluamide was obtained as a crystalline substance melting at 151°. For confirmation it was analysed with the following result :

0.1935 gm. substance gave 0.0213 gm. nitrogen,

N = 11.01% (calc. 11.38%)

The writer wishes to express his sincere thanks to Professor M. Matsui, at whose suggestion the work was undertaken, for his constant encouragement.

The Electrolytic Reduction of o-Nitrobenzene Azophenol

By

Hidemaru Itomi

(Received October 18, 1929)

It is already known that o-nitrobenzeneazophenol changes into phenolphentriazol[1] when electrolytically reduced in an alkaline solution with an electrode having a moderate reducing power, such as nickel. In this reduction the azo-group and the nitro-group may be regarded as undergoing reduction first and then interacting with each other so as to form the triazol. The present work was carried out to learn the conditions under which the nitro-group only is reduced to the amido-group and the azo-group is left unaffected.

As is well known, copper has a specific action of catalytically reducing the nitro-group to the amido-group, so copper was first chosen as the cathode, and an alkaline solution of o-nitrobenzeneazophenol was electrolysed with it. The cathode solution containing 2 grams of the azophenol in 150 c.c. of 4% caustic soda solution was electrolysed for $2\frac{1}{2}$ hours by passing a current of 2 amperes at 30°. After the electrolysis was over, the solution was neutralysed with sulphuric acid, evaporated nearly to dryness and then treated with ether to extract the azophenol that remained unchanged. On recrystallising the residue from boiling dilute alcohol, dark brown needle crystals were obtained with a yield of about 60%. They melted at 221–222° and showed all the properties of phenolphentriazol.

An acidic solution was next tried by using an alcoholic solution which contained 2 grams of o-nitrobenzeneazophenol in 200 c.c. of alcohol acidified with 30 c.c. of 10% sulphuric acid. A current of

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1 K. Elbs u. Keipler: J. prak. Chem., **67**, 580 (1903)

4·5–5·5 amperes was passed for 3 hours at 70–75°. During the electrolysis, the colour of the cathode solution gradually changed from red to dark brown, dark blue, yellow and finally to pink. The current was cut, and the solution was evaporated to drive off alcohol, when the o-nitrobenzeneazophenol that still remained unchanged crystallised out. It was filtered, and on cooling the filtrate a substance crystallising in scaly form was precipitated. As this substance was soon perceived to be the sulphate of some organic base, its concentrated aqueous solution was treated with barium carbonate, and the free base thus isolated was recrystallised from water as a dark brown crystal. The yield was found to be about 10%. It melted at 183–184° and dissolved easily in acetone, ether and alcohol, but with difficulty in benzene. It was amphoteric, dissolving in hydrochloric acid with a magenta colour, in conc. sulphuric acid with a dark green colour and in alkali with a dark brown colour. These properties all well agree with those of o-amidobenzeneazophenol.

The electrolysis was repeated under the same conditions, except that the current strength was decreased to 2–5 amperes and as a consequence the temperature was lowered to 40–50°. In this case the sulphate of o-amidobenzeneazophenol was produced only in very small quantity yielding phenolphentriazol as the chief reduction product.

It thus became apparent that the electrolytic reduction of o-nitrobenzeneazophenol into the corresponding amidocompound at a copper cathode could be brought about only by using an alcoholic sulphuric acid solution as the cathode solution and maintaining both current density and temperature high.

Next, lead was chosen as the cathode as having strong reducing power, and the electrolysis in the alkaline and acid solutions was studied. Two grams of o-nitrobenzeneazophenol were dissolved in 150 c.c. of 4% caustic soda solution, and the solution was electrolysed with a lead cathode of about 105 sq. cm. by passing a current of 2 amperes at 18° a little longer than 2 hours. After the electrolysis the cathode solution was neutralysed with sulphuric acid and treated with ether in order to dissolve unchanged o-nitrobenzeneazophenol. The residue obtained by evaporating the solution nearly to dryness was extracted with absolute alcohol, and the alcoholic extract was recrystallyzed from water. Thus o-amidobenzeneazophenol melting at 183–184° was obtained with a yield of 25%.

A quite unexpected result was obtained when the electrolysis was

conducted with a current of greater strength (3 5–4 amperes) at a higher temperature (60–70°) keeping the other conditions just the same as in the previous experiment. After the current had been passed for nearly $1\frac{1}{2}$ hours the dark coloured cathode solution was neutralised with sulphuric acid, and a gelatinous precipitate thus separated out was purified by crystallising it from hot alcohol. Greyish needle crystals showing all the properties of phenolphentriazol were isolated with a yield of about 50%. This result is just contrary to that obtained with a copper electrode in an acid solution.

The reduction experiment was also carried out in an acid solution containing 3 gr. of o-nitrobenzeneazophenol in the mixture of 200 c c. of alcohol and 40 c c. of 10% sulphuric acid. A lead plate of about 130 sq. cm. was taken as the cathode and a current of 2 amperes was passed at 21° for 4 hours. As the electrolysis went on some glittering crystals, which were afterwards identified to be o-amidobenzeneazophenol sulphate, begun to separate out in the solution. The yield was 25%. The yield could be raised to 45% by increasing the current strength to 3.5 amperes and at the same time raising the temperature to 60–70°.

Finally, to find the catalytic influence of copper and tin on this reduction, two experiments with the acid solution were conducted. To the cathode solution consisting of 2 grams of o-nitrobenzeneazophenol, 40 c c. of 10% sulphuric acid, 150 c c. of alcohol and 1 gram of crystalline copper sulphate were added, and this solution was electrolyzed with a current of 3 amperes at 50–60° for about 2 hours. The cathode solution gradually changed to a yellow colour, and some copper was seen floating on it.

The solution being treated in the manner described before, o-amidobenzeneazophenol was obtained with a yield of 50%. The remarkable catalytic action of copper on the reduction of o-nitrobenzeneazophenol will be clear if we compare the above result with that in the electrolysis conducted with a lead or copper electrode. The catalytic action exerted by tin was found to be still greater. In the experiment which was conducted exactly in the same way as in the above, except that 1 gram of $SnCl_2 2H_2O$ was substituted for the copper salt, the yield of o-amidobenzeneazophenol was found to be as high as 75%.

It was also observed, from the colour change of the cathode solution, that the electricity required for the reduction of 2 grams of the azophenol was 6.4 ampere-hours when copper was used as the

catalyst, while only 4.5 ampere-hours were sufficient when tin was substituted for copper.

Summary

1 Electrolytic reduction of o-nitrobenzeneazophenol was studied with the object of obtaining the corresponding amido-compound with the best yield.

2 Both alkaline and acid solutions were electrolyzed copper and lead being used as the cathode, and the conditions favourable for producing amidobenzeneazophenol were sought.

3 As a result of the research, an acidic cathode solution to which some stannous chloride has been added was found to give the best yield, when it is electrolyzed with a lead cathode at about 50–60°.

The author takes this opportunity to thank Professor Motooki Matsui at whose suggestion the work was carried out.

On the Ternary Silver Alloys

I. The System of Silver, Copper and Zinc

By

Shûzô Ueno

(Received October 23, 1929)

The ternary system of silver, copper and zinc seems not to have been studied hitherto and therefore an attempt was made, as described below, to fill in the blank.

I On the Binary Systems, Copper-Silver, Copper-Zinc and Silver-Zinc

For the copper and silver system, T. Hirose's[1] equilibrium diagram, and for the copper-zinc system, D. Iitsuka's[2] one, were adopted without any modification. With regard to the silver and zinc system, however, Petrenko's[3] latest diagram had to be slightly modified, not in respect of the nature of the equilibrium but in the form of the curves representing the liquidus, solidus or solubility. These must naturally have resulted because of differences in the working conditions. The modifications so tried are given in Fig. 1 in dotted lines, the data used being summarised in Tab. 27.

II Preliminary Experiments

The copper and the silver used as materials were both electrolytically pure, while the zinc was not so pure, yet of Merck's best quality. In order to avoid changes in the composition by volatilization, the silver was first fused under molten sodium chloride in a porcelain

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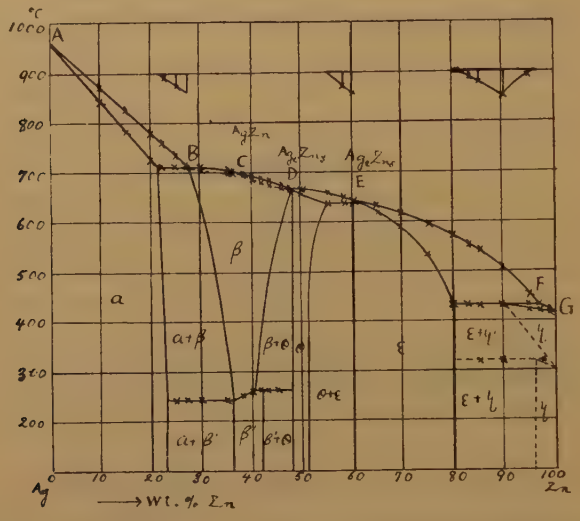
1 Report of the Imperial Mint, Osaka, No. **1**, 1 (1927)

2 These memoirs, VIII, 180 (1925); Metallkunde **19**, 396 (1927)

3 Zeits. Anorg. C. **165**, 297 (1927)

crucible, and while it was kept at temperatures a little higher than its melting point, the zinc and the copper were thrown in piece by piece and well stirred. The alloys thus prepared generally underwent

Fig. 1



a very slight loss and were found on analysis to contain 0.3%—0.5% Zn short of the given compositions. The experiments were made on the alloys as shown in Table 1.

Tab. 1

Metals taken in %		Metals analysed in %		Loss of Zn
Cu	Ag	Cu	Ag	in %
70	20	70.11	20.20	0.31
40	50	40.09	50.25	0.34
20	70	20.06	70.22	0.28
10	80	10.02	80.16	0.18
70	10	70.31	10.04	0.35
10	70	10.04	70.36	0.40
60	10	60.38	10.04	0.42
50	20	50.20	20.08	0.28
40	30	40.22	30.17	0.39
30	40	30.20	40.28	0.48
20	50	27.15	50.37	0.52
10	60	10.04	60.21	0.25
55	5	55.30	5.03	0.33
50	10	50.29	10.06	0.35

Through the microscopical examination of these alloys, the author came roughly to the conception that there is no field consisting of three phases, but that the β solid solution of the Cu-Zn system unites with β of the Ag-Zn system, and ε of the Cu-Zn system with ε of the Ag-Zn system, so that there are formed two wide homogeneous fields, secluded by which there would remain three heterogeneous fields in the triangular base. Such a conception was confirmed by further investigation, as will be described later.

Tab. 1 (cnotinued)

Metals taken in %		Metals Analysed in %		Loss of Zn
Cu	Ag	Cu	Ag	in %
40	20	40.26	20.14	0.40
25	35	25.23	35.19	0.42
15	45	15.19	45.28	0.47
5	55	5.09	55.46	0.55
10	40	10.04	40.16	0.20
35	15	35.13	15.05	0.18
25	25	25.20	25.18	0.38
15	30	15.09	30.18	0.27
10	35	10.06	35.23	0.29
5	25	5.04	25.23	0.27
10	20	10.12	20.23	0.35
15	10	15.17	10.11	0.28
10	10	10.13	10.17	0.30
10	15	10.14	15.21	0.35
5	5	5.17	5.25	0.42
5	70	5.03	70.28	0.31
„	„	5.04	70.28	0.32
„	„	5.05	70.33	0.38
„	„	5.07	70.26	0.33
„	„	5.03	70.31	0.34
„	„	5.11	70.25	0.36
„	„	5.05	70.16	0.21
„	„	5.07	70.25	0.32
„	„	5.02	70.33	0.35
„	„	5.09	70.28	0.37
„	„	5.15	70.18	0.33

III Cooling Curves

Each alloy weighed 20 gms, to which some more zinc was added to compensate for the loss through volatilization. No chemical analysis was made except for those given in Tab. I. All the alloys were directly fused in an electric furnace and thermally analysed by means of a Pt-Pt. Rh couple carefully calibrated.

IV Sectional-Diagrams

In order to establish the ternary equilibrium diagram, it was necessary first to get a number of sectional diagrams. The results of investigation are given below.

1 10% Zn-Section

The alloys of the compositions given in Tab. 2 were selected along the sectional line of 10% Zn. They were thermally analysed, the results of the analysis being given in Tab. 2.

With these results, the sectional diagram, Fig. 2, is plotted, where the liquidus AC represents the primary separation of α, BC that of a, and in the solidus $aa'Cb'b$ aa' stands for the complete crystallization of α, bb' that of a, and $a'C$ and $b'C$ that of the binary eutectic $(\alpha+a)$.

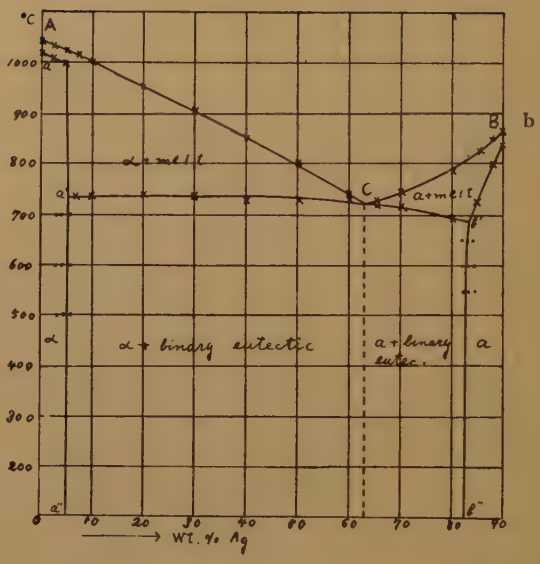
The binary eutectic point C lies at 10% Zn, 63% Ag and 27% Cu, where the three phases α, a and the melt form a monovariant system.

The solid phases with the composition marked with the black spots were annealed for a few hours at the corresponding temperatures and quenched, and were then microscopically tested for their structures,

Tab. 2

Alloy No.	Wt.-%			°C	
	Ag	Cu	Zn	Liquidus	Solidus
1	—	90	10	1040	1020
2	2	88	„	1035	1005
3	5	85	„	1022	999
4	7	83	„	1013	733
5	10	80	„	999	734
6	20	70	„	948	735
7	30	60	„	900	735
8	40	50	„	845	728
9	50	40	„	795	727
10	60	30	„	735	725
11	65	25	„	728	720
12	70	20	„	740	714
13	80	10	„	785	695
14	85	5	„	825	725
15	88	2	„	850	800
16	90	—	„	865	845

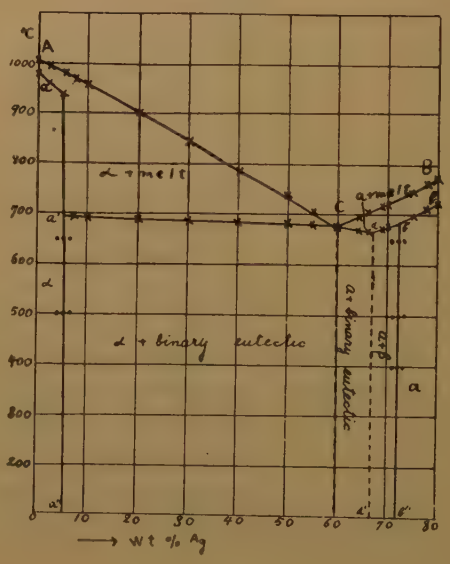
Fig. 2



Tab. 3

Alloy No.	Wt.-%			C°	
	Ag	Cu	Zn	Liquidus	Solidus
17	—	80	20	1000	978
18	2	78	„	990	960
19	5	75	„	975	945
20	7	73	„	966	690
21	10	70	„	952	692
22	20	60	„	900	693
23	30	50	„	844	689
24	40	40	„	790	684
25	50	30	„	742	688
26	55	25	„	710	686
27	60	20	„	681	680
28	64	16	„	698	676
29	66	14	„	706	672
30	69	11	„	712	673
31	70	10	„	720	680
32	75	5	„	745	700
33	78	2	„	760	715
34	80	—	„	772	725

Fig. 3



and in accordance with those results the solubility curves were drawn as shown in the same diagram.

2 20% Zn-Section

The alloys shown in Tab. 3 were used for the establishment of the 20% Zn-sectional diagram. The results of the thermal analysis are given with them in the same Table. The sectional diagram, Fig. 3. is drawn from the data just given.

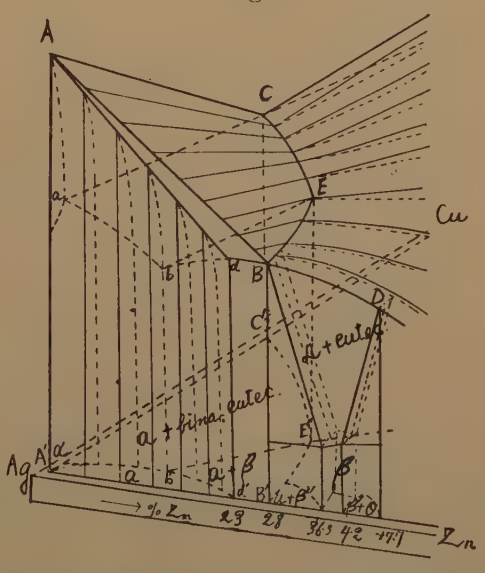
The liquidus *ACB* has the same meaning as that given in the 10% Zn sectional diagram. The solidus *aa'Cdb'b* differs however from it in this :— 1) *Cd* represents the crystallization of the binary eutectic a+*α*, 2) *db'* represents the crystallization of the binary complex *α*+*β*. The binary eutectic point *C* lies at 20% Zn, 60% Ag and 20% Cu, where the three phases *α*, a and the melt are in equilibrium.

3 The Silver Corner containing over 70% Silver

The liquidus and the solidus were first determined, and the solubility curves were then drawn according to the quenched structures.

For the purpose of quenching, 30 gms. of each of the required alloys were prepared, cut in pieces, and annealed for a few hours at definite temperatures, at which each alloy was thrown into water. The temperatures of quenching and the corresponding structures are here omitted in order to make the paper not too voluminous, but according to these data, the silver-corner diagram was drawn as shown in Fig. 4.

Fig. 4



Though the homogeneous solid solution at the silver side in the silver-copper system shows a tendency for the eutectic to be segregated by the low temperature annealing, this property is so markedly lessened by the addition of the zinc that the ternary alloys containing over 10% Zn no longer show any tendency towards segregation, however long they may be annealed. The temperature of the binary eutectic of silver and copper is depressed from 776° to

670° in relation to the amount of zinc added. This relation is represented by the curve *CE* along which the equilibrium of the three phases *a*, *a* and the melt is established.

Now turning to the Ag-Zn system, these metals from a series of silver-rich solid solutions *a*, in which the copper comes to be dissolved to the amount of 7.7% and forms a series of ternary solid solutions also named *a*. The binary solid solution *a* reacts also with the melt at 710° along the horizontal line *dB*, where the binary peritectic reaction, Liq.+a$\rightleftarrows\beta$, comes to proceed. This reaction is prolonged to the ternary melt, the temperature of which is depressed to 670° with the increase in the copper added. This relation is represented by the curve *BE* along which *a*, β and the melt are in equilibrium. The binary eutectic curve *CE* and the peritectical line *BE* vanish at a point *E*, which was found to lie at 61.7% Ag, 15% Cu and 23 3% Zn by combining a point *d* in the 20% Zn-section and another point *d* in 70% Ag-section, as will be described afterwards. The curve *Eb* is a boundary line between a surface *abECa* showing the binary eutectic reaction and a surface *EbdBE* showing the binary peritectic reaction.

The microstructure of the binary eutectic field is easily to be distinguished from that of the binary peritectic field in so far as they are mutually remote from the line *bE* Cp. Photo 4: (a+Eutec.) and Photo 10: ($a+\beta$). Closer to the curve *bE*, both structures become so much more similar, that it is practically impossible for them to be discriminated, although cooling curves given in the 20% Zn-section show clearly the existence of such differences. The fields recognizable at ordinary temperatures are therefore as follows:

1 $a'b'd'A'a'$: the structure being a
2 $a'b'E'C'a'$: the structure being $a+$eutec.
3 $b'E'B'd'b'$: the structure being $a+\beta$

4 30% Zn-Section

The alloys shown in Tab. 4 were used for the investigation of the 30% Zn-section, the results of which are given in the same table. The sectional diagram, Fig. 5, is drawn on the basis of the data just given.

The liquidus consists of two parts, of which *AC* stands for the separation of *a*, and *BC* for that of β. The solidus consists also of several branches, of which: 1) *aa'* stands for the complete cry-

Tab. 4

Alloy No.	Wt.-%			°C			
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic	Transformation
35	—	70	30	948	913	—	—
36	2	68	„	936	900	—	—
37	5	65	„	920	680	—	—
38	10	60	„	896	676	—	—
39	20	50	„	835	674	—	—
40	24	46	„	815	673	—	—
41	25	45	„	810	671	—	—
42	27	43	„	800	—	775	—
43	30	40	„	780	—	765	—
44	35	35	„	750	—	743	—
45	40	30	„	725	722	—	—
46	50	20	„	684	675	—	—
47	60	10	„	680	675	—	—
48	65	5	„	690	682	—	241
49	70	—	„	709	705	—	242

curves obtained with the alloys containing below 5% Cu.

5 35% Zn-Section

The alloys given in Tab. 5 were used for the investigation of the 35% Zn-section, the results of which are given in the column following the composition of the alloys in the same table.

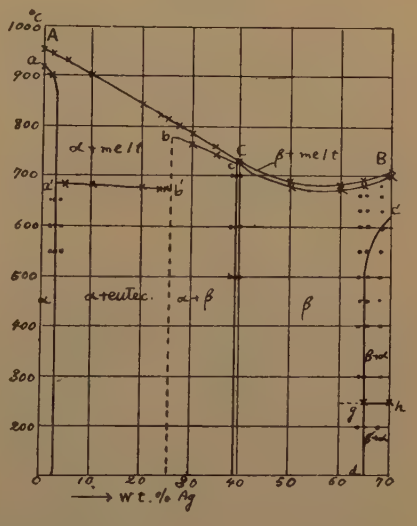
The sectional diagram, Fig. 6, is drawn on the basis of these data.

The binary peritectic reaction, Liq. $+\alpha \rightleftarrows$ Liq. $+\beta$, in the copper-zinc system is continued in the ternary system, in consequence of which β is separated along the curve aC, the point C being at 17% Ag, 35% Zn and 48% Cu, where the three phases α, β and the melt are in equilibrium. The curve $a'a''$ shows the solubility of β in α as was determined by the quenching method.

stallization of α; 2) $a'b'$ stands for that of the binary eutectic $a+\alpha$; 3) bc stands for that of the binary complex $\alpha+\beta$ due to the peritectic reaction Liq. $+\alpha \rightleftarrows$ Liq. $+\beta$ in the Cu-Zn system.

The segregation of α from β takes place along the curve $c'd$ due to the decrease in solubility on the temperature being lowered. The curve gh corresponds to the transformation of β into β', which is perceptible through the cooling

Fig. 5



Tab. 5

Alloy No.	Wt.-%			°C			
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic	Transformation
50	—	65	35	910	—	891	—
51	5	60	„	885	—	870	—
52	10	55	„	860	—	850	—
53	15	50	„	833	828	829	—
54	20	45	„	808	800	—	—
55	30	35	„	760	751	—	—
56	40	25	„	710	700	—	—
57	50	15	„	684	675	—	—
58	60	5	„	689	681	—	—
59	63	2	„	697	689	—	245
60	65	—	„	705	700	—	240

though no such breaks could be observed in the author's cooling curves.

7 45% Zn-Section and 50% Zn-Section

The compositions of the alloys and their thermal data with regard to these two sections are given in Tables 7 and 8.

The sectional diagrams, Figs. 8 and 9 are drawn on the basis of these data.

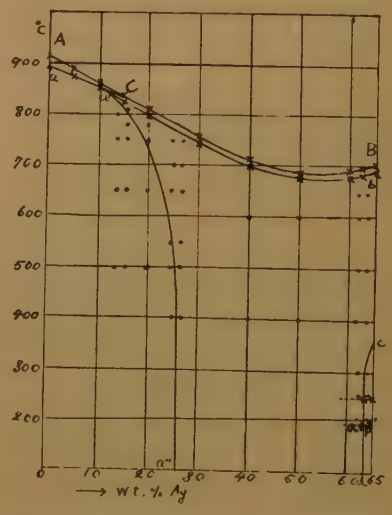
The changes in solubility on the temperatures being lowered are represented by cd with respect to the segregation of θ from β in 45% Zn-section and $a'S'S'$ with respect to that of γ from β in 50% Zn-section.

6 40%Zn-Section

The alloys used are given in Tab. 6, in which the results of the thermal analysis are co-tabulated.

The sectional diagram drawn on the basis of these data is shown in Fig. 7, where the dotted lines cd and $c'd'$ are provisionally drawn to show the transformation, $\beta \rightarrow \beta_1 \rightarrow \beta_2$ in the binary Cu-Zn system,

Fig. 6



8 55% Zn-Section

The alloys used and their thermal data are given in Tab. 9, on the basis of which the sectional diagram, Fig. 10, is drawn.

The liquidus AC and the solidus aS represent the separation of β, while the liquidus BC and the solidus bS show that of γ. The solidus bc is due to the peritectic reaction, Liq. $+\theta \rightleftarrows \varepsilon$, belonging to the Ag-

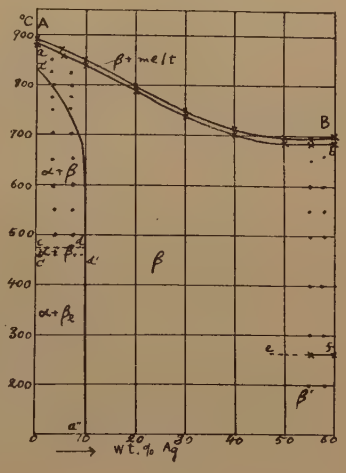
Tab. 6

Alloy No.	Wt.-%			°C			
	Ag	Cu	Zn	Liquidus	Solidus	Transformation 1	Transformation 2
61	—	60	40	890	884	460?	—
62	5	55	„	870	862	—	—
63	10	50	„	849	842	—	—
64	20	40	„	797	788	—	—
65	30	30	„	749	739	—	—
96	40	20	„	705	697	—	—
67	50	10	„	684	678	—	—
68	55	5	„	689	781	264	—
86	60	—	„	695	585	260	—

easily to be determined. The changes in solubility on the temperatures being lowered are represented by $a'S$ with respect to the separation of γ from β and SS' with respect to that of β from γ. The saturating-point of γ in β is shown by S, a point with the concentration of 5% Ag, 55% Zn and 40% Cu.

Zn system, while the curve SC refers to the separation of γ due to the peritectic reaction, Liq. $+\beta \rightleftarrows$ Liq. $+\gamma$, in the Cu-Zn system. The solid solution θ becomes identical to γ when the amount of copper attains a definite proportion which is however not

Fig 7.



Tab. 7

Alloy No.	Wt.-%			°C			
	Ag	Cu	Zn	Liquidus	Solidus	Transformation 1	Transformation 2
70	—	55	45	883	873	471	460?
71	5	50	„	860	852	—	—
72	10	45	„	837	827	—	—
73	21	35	„	785	777	—	—
74	30	25	„	733	724	—	—
75	40	15	„	697	687	—	—
76	50	5	„	678	672	—	—
77	52	3	„	677	671	263	—
78	55	—	„	679	670	261	—

Tab. 8

Alloy No.	Wt.-%			°C			
	Ag	Cu	Zn	Liquidus	Solidus	Transformation 1	Transformation 2
79	—	50	50	868	862	471	460
80	5	45	„	845	833	—	—
81	10	40	„	820	805	—	—
82	20	30	„	772	756	—	—
83	30	20	„	716	705	—	—
84	40	10	„	681	673	—	—
85	50	—	„	668	656	—	—

Fig. 8

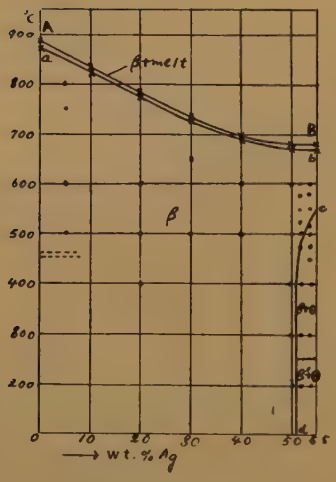
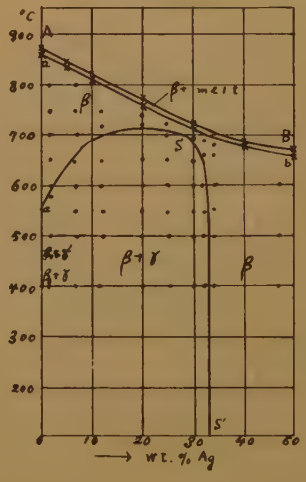


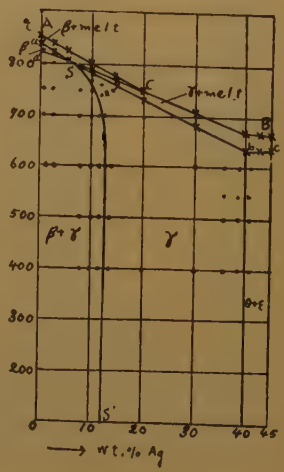
Fig. 9



Tab. 9

Alloy No.	Wt.-%			°C		
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic
86	—	45	55	853	841	—
87	2	43	„	831	825	—
88	5	40	„	825	808	—
89	10	35	„	800	783	790
90	15	30	„	775	757	762
91	20	25	„	750	735	745
92	23	22	„	735	717	732
93	30	15	„	703	680	—
94	40	5	„	662	630	—
95	43	2	„	657	633	—
96	45	—	„	655	635	—

Fig. 10



9 The Equilibrium-Diagram for 0–55% Zn including the Copper-rich Side

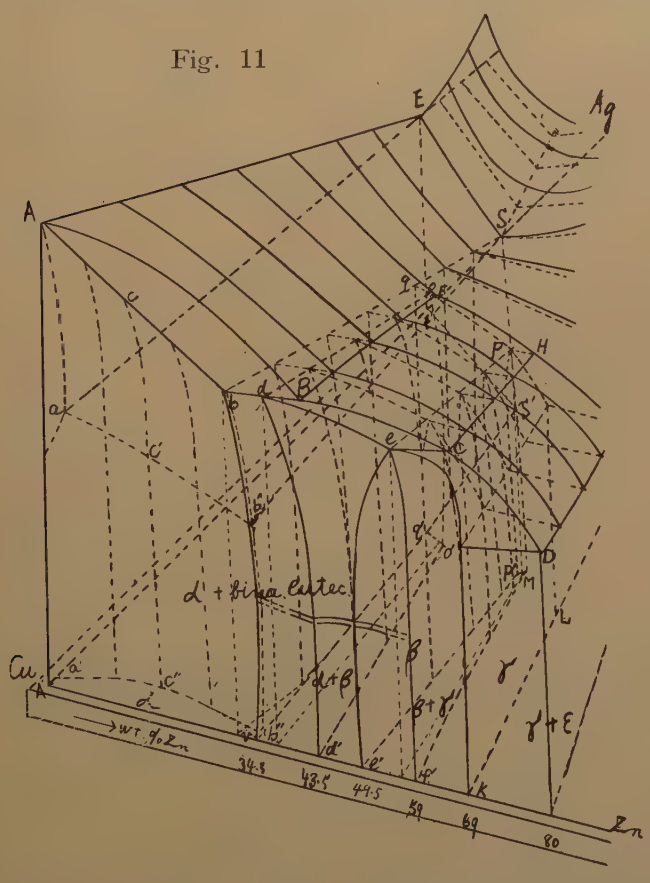
The thermal analysis as well as the quenching method was used in order to establish this equilibrium, as a results of which the diagram, Fig. 11, was drawn.

The surface *ABSEA* represents the liquidus of α and the surface *ab'SEa* the solidus of a binary eutectic $\alpha+\alpha$.

The copper-rich solid solution in the Cu-Zn system dissolves silver to the extent of 5.5% and produces a ternary solid solution α, the solidus of which is represented by the surface *Acbb'c'aA*.

The horizontal line *bB* stands for the peritectic reaction, Liq.+$\alpha \rightleftarrows$Liq.+β, at 890° in the Cu-Zn system. The temperature of the reaction is depressed on the addition of silver, as it finally attains the position of a point *F* on a curve *BF* representing the peritectical reaction due to the Cu-Zn system, as the following equation shows:- Liq.+$\alpha \rightleftarrows$Liq.+β. This line vanishes at about 38% Ag, 32% Zn and 30% Cu, where β dissolves α completely, as the surface *bB-Fq* shows.

Fig. 11



The surface *dd'o'od* is a solubility surface of β in α originating from the curve *dd'* in the Cu-Zn system. This fact is confirmed by the following experiment:—An alloy of 5% Ag, 40% Zn and 55% Cu, quenched at 600°, was seen to have a bistructure consisting of $\alpha+\beta$ (Photo 13),

while, when quenched at 820°, it becomes homogeneous: (Photo 14). The solid solution β becomes saturated with α along the curve *do*, which corresponds to the point *d* in the Cu-Zn system. The liquidus of β is shown by *SBCH* and the solidus by *SqodeP*, but they extend so much further that they can not completely be drawn within the space occupied by Fig. 11.

The horizontal line *eC* represents the peritectic reaction in the Cu-Zn system at 830°: Liq. $+\beta \rightleftarrows$ Liq. $+\gamma$. Its temperature falls on the silver being increased, as shown by the curve *CH*. This peritectical line vanishes at about 36% Ag, 13% Cu and 51% Zn, where all comes to be dissolved in β, as the surface *ecHP* shows. The γ, which is produced by this reaction, solidifies at the surface *eKLPe*: Cp. Photo 22. The solid solution β segregates γ along the surface *ec'p'pe* on the temperature being lowered, due to the decrease in solubility. An alloy with 2% Ag, 55% Zn and 43% Cu, when quenched at 600° shows the structure $\beta+\gamma$: Cp. Photo 20. When quenched however at 820°, it turns homogeneous ($=\gamma$), as may be seen from Photo 21. The β is segregated from γ along the surface *cf'MPe* due to the decrease in solubility on the temperature being lowered. Thus, we get in this corner six fields at room temperature:

1 *a'C''b''qA'a'*: the structure being α
2 *a'c''b''S'E'a'*: the structure being α + eutec.
3 *vb''d'o'q'b''V*: the structure being $\alpha+\beta$
4 *S'q'o'd'e'P'*: the structure being β
5 *e'P'Mf'e'*: the structure being $\beta+\gamma$
6 *Mf'KL*: the structure being γ

10 60% Zn-Section

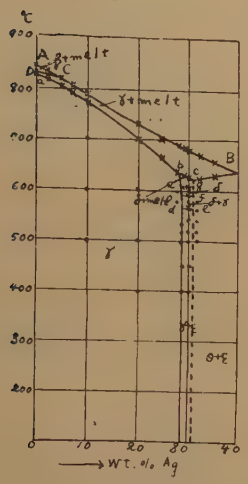
The composition of the alloys used and their thermal data are given in Tab. 10.

Tab. 10

Alloy No.	Wt.-%			°C				
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic	Seperation of ε or γ from δ	Eutectoidal transformation
97	—	40	60	838	825	830	—	—
98	2	38	„	830	817	826	—	—
99	5	35	„	815	801	808	—	—
100	7	33	„	803	788	—	—	—
101	10	30	„	785	777	—	—	—
102	20	20	„	729	705	—	—	—
103	25	15	„	700	660	—	—	—
104	28	12	„	685	635	—	—	—
105	29	11	„	680	611	627	—	—
106	30	10	„	675	610	623	590?	562?
107	32	8	„	664	—	622	—	—
108	35	5	„	650	628	—	—	
109	40	—	„	637	—	636	—	—

The sectional diagram drawn on the basis of the data is given in Fig. 12, where the liquidus AC stands for the separation of β, and BC for that of γ. There take place two binary peritectic reactions belonging to the Cu-Zn system, one of which is Liq.$+\beta \rightleftarrows$Liq. $+\gamma$, and as its result γ is separated along the curve DC, while the other is Liq.$+\gamma \rightleftarrows$ Liq.$+\delta$, and as its result δ is separated along the curve bc. There takes place also in the Ag-Zn system a peritectic reaction :— Liq.$+\theta \rightleftarrows \varepsilon$, ε of which is separated along the curve Bc. The crystallization of γ takes place along the solidus ab, that of δ along $a'g$ and that of the binary complex $\gamma+\varepsilon$ due to the binary peritectic reaction, Liq.$+\theta \rightleftarrows \varepsilon$, in the Ag-Zn system along Bc. The curve of corresponds to the separation of γ from δ, and the curve dc shows the eutectoidal transformation, $\delta \rightleftarrows \gamma+\varepsilon$, in the Cu-Zn system.

Fig. 12



11 65% Zn-Section

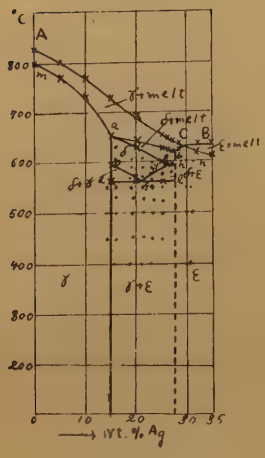
The alloys used and their thermal data are given in Tab. 11.

Tab. 11

Alloy No.	Wt.-%			°C					
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic 1	Peritectic 2	Separation of γ or ε from δ	Eutectoidal transformation
110	—	35	65	827	800	—	—	—	—
111	5	30	„	800	770	—	—	—	—
112	10	25	„	768	730	—	—	—	—
113	15	20	„	730	—	650	—	595	560
114	20	15	„	694	627	640	—	570 ?	561
115	22.5	12.5	„	675	615?	635	—	570 ?	561
116	25	10	„	659	600	623	—	—	560
117	26	9	„	650	—	622	595	—	—
118	27	8	„	642	—	621	595	—	—
119	28.5	6.5	„	635	—	624	—	—	—
120	30	5	„	630	627	—	—	—	—
121	32	3	„	633	612	—	—	—	—
122	35	—	„	633	611	—	—	—	—

On the basis of these data, the sectional diagram, Fig. 13, is drawn, in which the liquidus AC stands for the separation of γ and BC for

Fig. 13



that of ε. The solidus *maghbCn* consists of several branches, of which *ma* stands for the solidification of γ; *ag* for that of δ; *gh* for the binary peritectic reaction, Liq. $+\delta \rightleftarrows \varepsilon$, in the Cu-Zn system; *Cn* for the solidification of ε; and *bC* for that of the binary complex $\gamma+\varepsilon$ due to the binary peritectic reaction, Liq. $+\theta \rightleftarrows \varepsilon$, in the Ag-Zn system. The curve *de* results from the eutectoidal transformation, $\delta \rightleftarrows \gamma+\varepsilon$, in the Cu-Zn system. The curve *of* corresponds to the separation of γ and the curve *gf* to that of ε from δ. The three phases γ, δ and ε are in equilibrium at the point *f*.

12. 70% Zn-Section

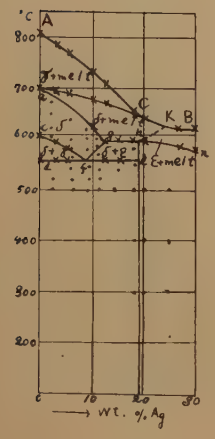
The alloys taken and their thermal data are given in Tab. 12.

Tab 12

Alloy No.	Wt.-%			°C					
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic 1	Peritectic 2	Separation of γ or ε from δ	Eutectoidal transformation
123	—	30	70	800	—	695	—	600?	556
124	3	27	„	780	677	690	—	587	557
125	5	25	„	765	665	682	—	580?	558
126	10	20	„	730	625	670	—	570	559
127	12.5	17.5	„	710	597	665	—	594	560
128	15	15	„	685	—	658	595	—	560
129	18	12	„	657	—	650	596	—	—
130	20	10	„	637	—	—	594	—	—
131	22.5	7.5	„	627	596	—	—	—	—
132	25	5	„	619	591	—	—	—	—
133	27.5	2.5	„	619	590	—	—	—	—
134	30	—	„	619	583	—	—	—	—

The sectional diagram is drawn in Fig. 14. It is quite similar to the previous diagram, except the part *ghk*, along which ε is separated due to the reaction, Liq. $+\delta \rightleftarrows$ Liq. $+\varepsilon$, in the Cu-Zn system. The data from the cooling curves were however not sufficient to fix the part *hk*, and therefore it is now provisionally shown with dotted lines.

Fig. 14



13 75% Zn-Section

The alloys taken and their thermal data are given in Tab. 13, and the sectional diagram drawn on the basis of these data is given in Fig. 15.

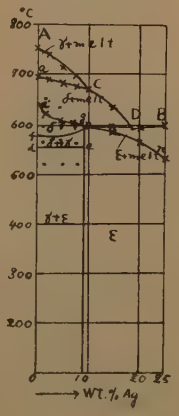
The liquidus AC corresponds to the separation of γ, CD to that of δ, and BD to that of ε. The solidus consists of two branches of which $a'g$ stands for δ and gn for ε. The δ is separated along the curve aC due to the binary peritectic reaction, Liq.$+\gamma \rightleftarrows$Liq.$+\delta$, in the Cu-Zn system. The point C lies at 10% Ag, 75% Zn and 15% Cu, where the three phases γ, δ and the melt are in equilibrium. Along the curve gD, ε is separated due to the binary peritectic reaction, Liq.$+\delta$

Tab. 13

Alloy No.	Wt.-%			°C					
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic 1	Peritectic 2	Separation of ε from δ	Eutectoidal transformation
135	—	25	75	750	650	695	—	575?	556
136	2	23	„	742	615	691	—	575	556
137	5	20	„	714	600	683	—	576	557
138	7.5	17.5	„	697	598	680	—	—	558
139	10	15	„	675	593	672	595	—	—
140	15	10	„	630	585	—	595	—	—
141	20	5	„	592	570	—	—	—	—
142	25	—	„	597	536	—	—	—	—

$\rightleftarrows$Liq.$+\varepsilon$, in the Cu-Zn system. The point C lies at 18% Ag, 75% Zn and 7% Cu, where the three phases γ, ε and the melt are in equilibrium. The curve fg shows the separation of ε from δ, while the dc has the same meaning as given in the previous section.

Fig. 15



14 80% Zn-Section

The alloys used and the thermal data are given in Tab. 14, and the sectional diagram is shown in Fig. 16.

This section is so similar to the previous one that it needs no more explanation.

Fig. 16

Tab. 14

Alloy No.	Wt.-%			°C		
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic
143	—	20	80	700	580	590
144	2.5	17.5	〃	685	581	591
145	5	15	〃	660	584	593
146	10	10	〃	610	585	596
147	15	5	〃	575	532	—
148	20	—	〃	570	435	—

15 98% Zn-Section

The alloys taken and the thermal data are given in Tab. 15, and the sectional diagram is given in Fig. 17.

Fig. 17

Tab. 15

Alloy No.	Wt.-%			°C			
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic 1	Peritectic 2
149	—	15	85	647	480	590	—
150	2.5	12.5	〃	620	480	592	—
151	5	10	〃	595	—	592	426
152	10	5	〃	557	—	—	428
153	15	—	〃	544	—	—	480

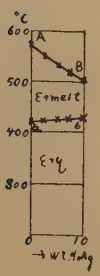
This section differs from the previous only in the part *bcd*, where ε solidifies along *bc* and η is separated along *cd* due to the binary peritectic reaction, Liq. $+\varepsilon \rightleftarrows \eta$, in the Cu-Zn system.

16 90% Zn-Section

The alloys taken and the thermal data are given in Tab. 16. and the sectional diagram is as shown in Fig. 18.

The curve *AB* represents the liquidus of ε, and *ab* the curve of separation of η' due to the binary peritectic reaction: Liq. $+\varepsilon \rightleftarrows \eta'$.

Fig. 18



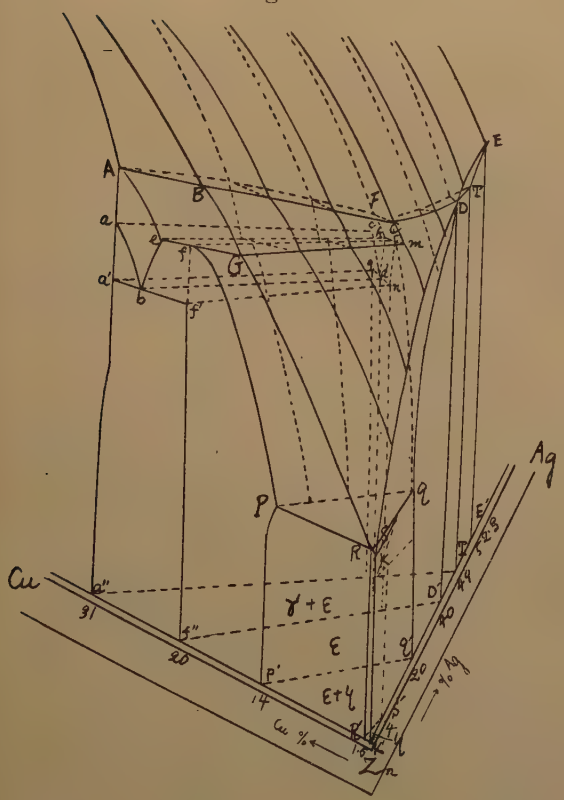
Tab. 16

Alloy No.	Wt.-%			°C	
	Ag	Cu	Zn	Liquidus	Peritectic
154	—	10	90	570	422
155	2.5	7.5	90	550	424
156	5	5	90	530	426
157	7.5	2.5	90	515	428
158	10	—	90	501	430

17 The Zinc Corner

In order to establish this corner-diagram, the cooling curves as well as the quenching data were used, as a result of which we have got the one given in Fig. 19.

Fig. 19



The horizontal line AB refers to the peritectic reaction, Liq.$+\gamma \rightleftarrows$Liq. $+\delta$, in the Cu-Zn system at 695°. The temperature of this reaction is depressed by the addition of silver from 695° to 620°, in accordance with which the curve BC makes its appearance to represent the ternary peritectical reaction. The horizontal line DT represents the binary peritectic reaction, Liq.$+\theta \rightleftarrows \varepsilon$, in the Ag-Zn system at 636°. The temperature is then depressed to 620° by the addition of copper, the relation of which is traced by the curve DC. An alloy with 28% Ag, 65% Zn and 7% Cu, which is a point in the curve

DC, was quenched at 550°, the structure of which is $\gamma+\varepsilon$, as shown in Photo 28. These two peritectical lines *BC* and *DC* meet at a point *C* with 26% Ag, 7% Cu and 67% Zn, which is the point of intersection of the peritectical line *BCD* and the curve *BC* connecting a point *d* in the 60% Zn and another *d* in the 65% Zn-section. The surface *ABCFA* corresponds to the former reaction and the surface *CFTDC* to the latter, while the surface *BGmcB* is the liquidus of δ.

The horizontal line *cG* shows the peritectic reaction, Liq.$+\delta \rightleftarrows$Liq. $+\varepsilon$, in the Cu-Zn system at 590°, the temperature being raised to 596° with the increase in copper. The ternary peritectical line on the addition of silver is given by *Gm*, which fades away near the point of 22% Ag, 5% Cu and 73% Zn. This reaction is shown by the surface *cGmhc*, in which *cfohc* is the solidus of the binary complex $\delta+\varepsilon$ and *fGmof* is the surface of the liquid which will solidify with the surface of *fpqof* on the temperature being lowered.

The surface *AchFA* is the solidus of the ternary δ which, being unstable, splits up on the one hand into γ on the surface *abdca*, and on the other into ε on the surface *ebdhc*. As to the field for the separation of γ from δ, an alloy with 6% Ag, 70% Zn and 24% Cu, quenched at 625°, becomes homogeneous ($=\delta$) as Photo 29 shows, but quenched at 565° it becomes heterogeneous ($=\delta+\gamma$) as Photo 30 shows. As to the separation of ε from δ, an alloy with 22% Ag, 65% Zn and 13% Cu, when quenched at 600° shows the δ-structure (Photo 26), but when quenched at 565°, it turns heterogeneous (Phot 27 : $\delta+\varepsilon$).

The horizontal line *a'f'* shows the eutectoidal reaction, $\delta \leftrightarrows \gamma+\varepsilon$, in the Cu-Zn system at 555° the temperature being raised to 562° with the increase in silver as shown by the curve *bd*. Though the line *a'f'* corresponds to a nonvariant reaction in the Cu-Zn system, the curve *bd* in the ternary system does not, there being only the three phases δ, γ and ε in equilibrium. The surface *a'f'nga'* corresponds to the binary eutectoidal : the structure under the surface consists therefore of $\gamma+\varepsilon$: see Photos 31 and 34. The surface *GRSDCmG* is the liquidus of ε, and *fPqDCof* is its solidus.

The horizontal line *PR* shows the binary peritectic reaction, Liq. $+\varepsilon \rightleftarrows \eta$, in the Cu-Zn system at 423°, while the horizontal line *q.S* shows the binary peritectic reaction, Liq.$+\varepsilon \rightleftarrows \eta$, in the Ag-Zn system at 430°. The temperature of the former reaction is raised by the addition of silver, while that of the latter is lowered by the addition

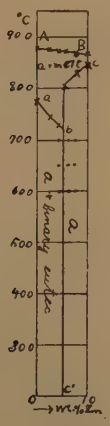
of copper, so that both the ternary reactions will be united at the temperatures between 423° and 430°. These binary peritectic reactions going on in the ternary system are shown by the surface *PQSRP*. The equilibrium between three phases, ε, η and the melt, is shown by the curve *RS*. The alloys at the zinc corner limited by a line connecting 4% Ag in the Ag-Zn and 1.4% Cu in the Cu-Zn, must therefore form a homogeneous field (η). In so far as this is concerned, we come to have four parts there at room temperatures:

1) $a''f'D'T'a''$: structure, $\gamma+\varepsilon$
2) $f''P'q'D'f''$: structure, ε
3) $P'q'S'R'P'$: structure, $\varepsilon+\eta$
4) $R'S'K'$: structure, η

18 90% Ag-Section

The alloys, and the thermal data are given in Tab. 17 and the sectional diagram in Fig. 20.

Fig. 20



Tab. 17

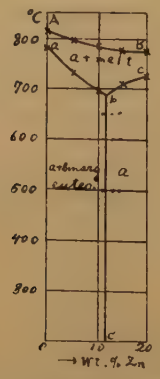
Alloy No.	Wt.-%			°C	
	Ag	Cu	Zn	Liquidus	Solidus
159	90	10	—	875	775
160	„	7.5	2.5	873	740
161	„	6	4	871	727
162	„	5	5	870	805
163	„	2.5	7.5	868	830
34	„	—	10	865	845

In this section there occurs crystallization, *AB* standing for the liquidus of the solid solution *a*, *ab* for the solidus of the binary eutectic $a+\alpha$, and *cbc'* for that of *a*.

19 80% Ag-Section

Alloys and thermal data, and the diagram are given in Tab. 18 and in Fig. 21.

Fig. 21



Tab. 18

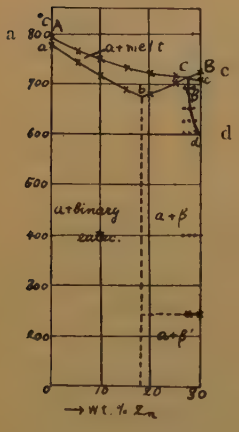
Alloy No.	Wt.–%			°C	
	Ag	Cu	Zn	Liquidus	Solidus
164	80	20	—	807	776
165	„	15	5	797	728
166	„	10	10	785	695
167	„	5	15	777	712
16	„	—	20	772	725

Exactly the same explanation applies here as in the previous section.

20 70% Ag-Section

The alloys and the thermal data are given in Tab. 19 and the diagram, in Fig. 22.

Fig. 22



Tab. 19

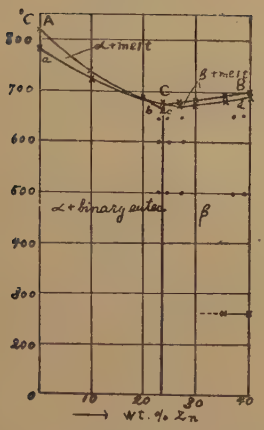
Alloy No.	Wt.–%			°C			
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic	Trans-formation
168	70	30	—	785	777	—	—
169	„	25	5	760	740	—	—
12	„	20	10	740	714	—	—
170	„	15	15	726	—	688	—
31	„	10	20	720	—	680	—
171	„	5	25	712	—	700	—
172	„	2	28	710	707	—	240
49	„	—	30	709	705	—	242

AC is the liquidus of α, BC that of β, ab the solidus for the binary eutectic $\alpha+\alpha$, Cc that for β, and bC that for the binary complex $\alpha+\beta$. The curve Cd shows the segregation of α from β.

21 60% Ag-Section

The alloys and thermal data are given in Tab. 20 and the diagram in Fig. 23.

Fig. 23



Tab. 20

Alloy No.	Wt.-%			°C		
	Ag	Cu	Zn	Liquidus	Solidus	Trans-formation
173	60	40	—	815	776	—
10	,,	30	10	735	725	—
27	,,	20	20	681	680	—
174	,,	17	23	672	670	—
175	,,	13	27	675	671	—
47	,,	10	30	680	675	—
58	,,	5	35	689	681	262
69	,,	—	40	695	685	260

The liquidus is represented by *AbCB*, in which *Abc* is for *α*, and *BC* for *β*. The solidus consists of two branches, of which *abc* is for the binary eutectic *α*+*α* and *cd* for *β*. At the point *b* there are three phases in equilibrium, i. e. *α*, *β* and the melt, just as described in connection with the 20% Zn-section.

22 50% Ag and 40% Ag-Sections

The compositions of the alloys and the thermal data of these two sections are given in Tables 21, and 22.

Tab. 21

Alloy No.	Wt.-%			°C	
	Ag	Cu	Zn	Liquidus	Solidus
176	50	50	—	851	776
9	,,	40	10	795	727
25	,,	30	20	742	688
177	,,	25	25	703	673
46	,,	20	30	684	675
57	,,	15	35	684	675
67	,,	10	40	684	678
76	,,	5	45	678	672
85	,,	—	50	668	656

Tab. 22

Alloy No.	Wt.-%			°C		
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic
178	40	60	—	887	776	—
8	,,	50	10	845	728	—
24	,,	40	20	790	684	—
179	,,	32	28	735	—	—
45	,,	30	30	725	722	—
56	,,	25	35	710	700	—
66	,,	20	40	705	697	—
75	,,	15	45	697	687	—
84	,,	10	50	681	673	—
94	,,	5	55	662	630	—
180	,,	2	58	645	—	635
109	,,	—	60	637	—	636

The sectional diagrams. Fig. 24 and 25, are drawn on the basis of these data.

Fig. 24

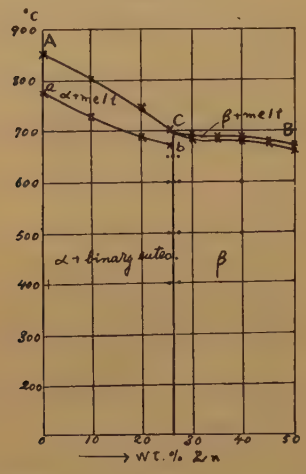
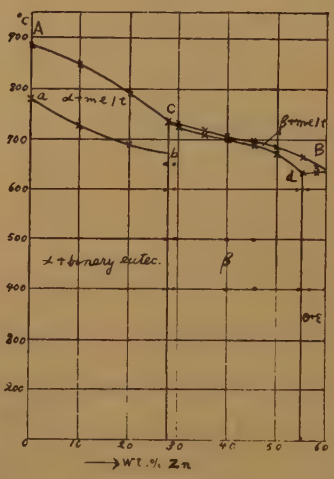


Fig. 25

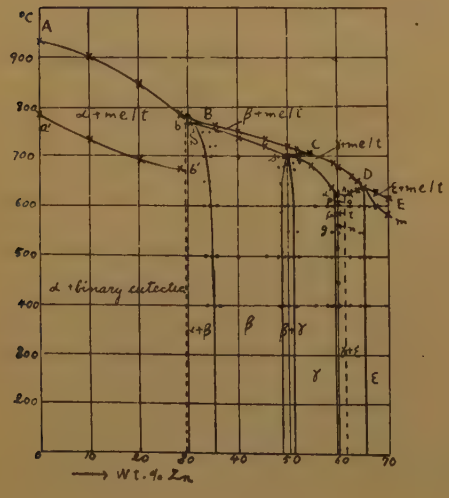


The same explanation applies here as given in the previous section except only that there is a new, curve dB in the 40% Zn-section, along which ε is separated, due to the binary peritectic reaction, Liq.$+\theta \rightleftarrows \varepsilon$, in the Ag-Zn system.

23 30% Ag-Section

The alloys and the thermal data are given in Tab. 23 and the diagram in Fig. 26.

Fig. 26



The liquidus consists of frour branches, of which AB is for α, BC for β, CD for r, and DE for ε. The solidus consists also of several branches, of which ab' is for the solidification of the binary eutectic $\alpha+a$, bS for that of the binary complex $\alpha+\beta$ due to the binary peritectic reaction, Liq.$+\alpha \rightleftarrows \beta$, in the Cu-Zn system, Ss for β, sd for γ, Pq for δ, and hd for the binary peritectic reaction, Liq.$+\theta \rightleftarrows \varepsilon$, in the Ag-Zn system. Along sC, γ is separated due to the binary

Tab. 23

Alloy No.	Wt.-%			°C				
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic	Separation of ε from δ	Eutectoidal transfomation
181	30	70	—	934	776	—	—	—
7	„	60	10	999	734	—	—	—
23	„	50	20	844	689	—	—	—
182	„	42	28	785	673	—	—	—
43	„	40	30	780	—	765	—	—
183	„	38	32	767	—	765	—	—
55	„	35	35	760	751	—	—	—
65	„	30	40	749	739	—	—	—
74	„	25	45	733	724	—	—	—
83	„	20	50	716	—	705	—	—
184	„	18	52	710	702	704	—	—
93	„	15	55	703	680	—	—	—
185	„	11	59	682	645	—	—	—
106	„	10	60	675	610	623	590 ?	562 ?
186	„	7	63	650	—	625	—	—
187	„	6	64	647	—	632	—	—
120	„	5	65	630	627	—	—	—
188	„	3	67	629	600	—	—	—
134	„	—	70	619	583	—	—	—

peritectic reaction, Liq. $+\beta \rightleftarrows$ Liq. $+\gamma$. Along *gn*, the binary complex $\gamma+\varepsilon$ is separated due to the binary eutectoidal transformation in the Cu-Zn system. Lastly, γ is separated from δ along the curve *ft*.

24 20% Ag and 10% Ag-Sections

The compositions of the alloys and the thermal data of these two sections are given in Tables 24 and 25.

The sectional diagrams, Figs. 27 and 28, are drawn on the basis of these data.

These two sections differ from the 30% Ag-section in the following

Tab. 24

Alloy No.	Wt.-%			°C					
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic 1	Peritectic 2	Separation of δ or ε from δ	Eutdctoidal transformation
189	20	80	- -	970	777	—	—	—	—
6	„	70	10	948	735	—	—	—	—
22	„	60	20	900	693	—	—	—	—
39	„	50	30	835	674	—	—	—	—
190	„	48	32	824	—	810	—	—	—
191	„	47	33	817	—	808	—	—	—
54	„	45	35	808	800	—	—	—	—
64	„	40	40	797	788	—	—	—	—
73	„	35	45	785	777	—	—	—	—
82	„	30	50	772	756	—	—	—	—
192	„	28	52	762	749	751	—	—	—
193	„	26	54	752	740	748	—	—	—
91	„	25	55	750	735	745	—	—	—
102	„	20	60	729	705	—	—	—	—
194	„	16	64	700	635	638	—	585	560
114	„	15	65	694	627	640	—	570 ?	561
195	„	13.5	66.5	680	610	640	—	588	560
196	„	13	67	675	—	636	595	—	561
130	„	10	70	637	—	—	594	—	—
141	„	5	75	592	570	—	—	—	—
148	„	—	80	570	435	—	—	—	—

Tab. 25

Alloy No.	Wt.-%			°C					
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic 1	Peritectic 2	Separation of ε or γ from δ	Eutectoidal transformation
197	10	90	—	1028	777	—	—	—	—
5	„	80	10	999	734	—	—	—	—
21	„	70	20	952	692	—	—	—	—
38	„	60	30	896	676	—	—	—	—
198	„	59	31	886	673	—	—	—	—
199	„	57	33	872	—	853	—	—	—
52	„	55	35	860	—	850	—	—	—
63	„	50	40	849	842	—	—	—	—
72	„	45	45	837	827	—	—	—	—
81	„	40	50	820	805	—	—	—	—
200	„	36	54	805	—	791	—	—	—
89	„	35	55	800	783	790	—	—	—
201	„	33	57	795	785	—	—	—	—
101	„	30	60	785	770	—	—	—	—
112	„	25	65	768	730	—	—	—	—
202	„	23	67	750	665	674	—	590	557
203	„	22	68	742	650	674	—	580	556
126	„	20	70	730	625	674	—	570	557
204	„	19	71	715	—	675	595	565	558
205	„	17	73	690	—	674	595	—	558
139	„	15	75	675	593	672	595	—	—
146	„	10	80	610	585	—	596	—	—
152	„	5	85	557	—	428	—	—	—
158	„	—	90	501	—	430	—	—	—

points: — δ is solidified along *de*, γ separated from δ along *ft*, ε separated from δ along *et*, the binary complex $\gamma+\varepsilon$ separated along

Eig. 27

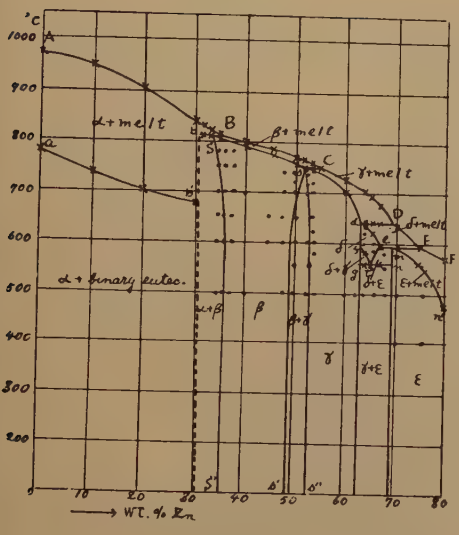
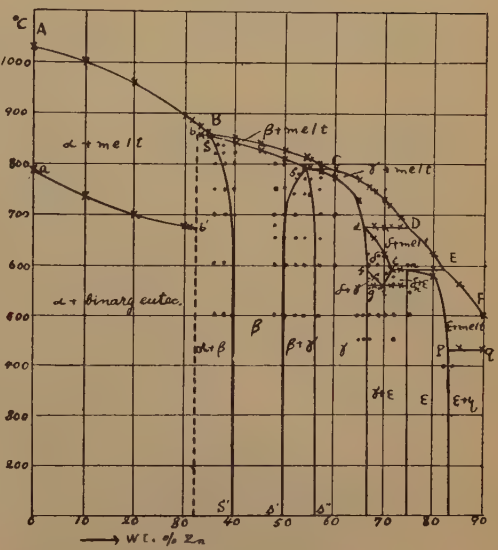


Fig. 28

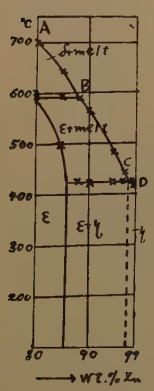


gh due to the reaction, $\delta \rightleftarrows \gamma + \varepsilon$, in the Cu-Zn system, and, lastly, ε separated along *eE* due to the binary peritectic reaction, Liq. $+ \delta \rightleftarrows$ Liq. $+ \varepsilon$, in the Cu-Zn system. The difference between the 10% Ag and the 20% Ag-section is, that a new curve *Pq* appears here, which corresponds to the binary peritectic reaction: Liq. $+ \varepsilon \rightleftarrows \eta$.

25 A Part of 1% Ag-Section

Finally, a part of 1% Ag-section was investigated in order to find out the relation of η in equilibrium. The alloys and the thermal data,

Fig. 29



Tab. 26

Alloy No.	Wt.-%			C°		
	Ag	Cu	Zn	Liquidus	Solidus	Peritectic
206	1	19	80	697	580	590
207	„	14	85	640	480	591
208	„	11	88	590	—	423
209	„	9	90	565	—	423
210	„	4	95	482	—	424
211	„	2	97	440	—	425
212	„	1	98	425	424	—
213	„	—	99	425	419	—

and the diagram are given in Tab. 26 and Fig. 29.

The curve *CD* is the liquidus and *Ce* the solidus of η. At the point *C*, three phases ε, η and the melt, are in equilibrium.

Tab. 27

Wt.-% Zn	°C			Peritectic Crystallization in Sec.	°C	Transformation in Sec.
	Liquidus	Solidus	Peritectic		Transformation	
10	865	845	—	—	—	—
15	822	780	—	—	—	—
20	772	725	—	—	—	—
22	760	—	710	20	—	—
25	730	—	710	60	240	10
27	715	—	709	80	241	20
30	709	705	—	—	242	70
35	705	700	—	—	240	150
36	703	700	—	—	240	160
38	700	697	—	—	250	130
40	695	685	—	—	260	120
42	689	686	—	—	263	150
43	687	684	—	—	262	100
45	679	670	—	—	261	100
47	668	665	—	—	—	—
50	668	656	—	—	—	—
55	655	—	635	20	—	—
58	647	—	636	60	—	—
60	637	—	636	100	—	—
65	633	611	—	—	—	—
70	619	583	—	—	—	—
75	597	536	—	—	—	—
80	570	435	—	—	—	—
83	555	—	430	20	—	—
85	544	—	431	50	320?	—
90	501	—	439	90	320	—
95	447	425	430	30	320	—
97	430	420	—	—	320?	—
99	425	419	—	—	—	—

28 The Complete Equilibrium-Diagram

With all the data above given, we were able to draw the iso-thermal (Fig. 30), the spatial (Fig. 31), and the projection diagram (Fig. 32).

Fig. 30

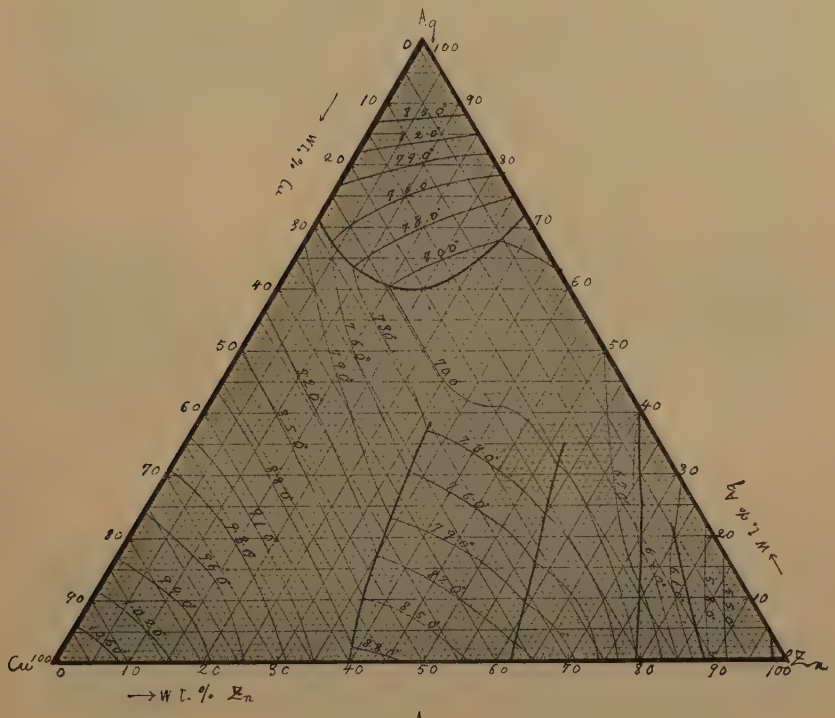

Ag
Wt. % Cu
Wt. % Ag
Cu
Zn
→ Wt. % Zn

Fig. 31

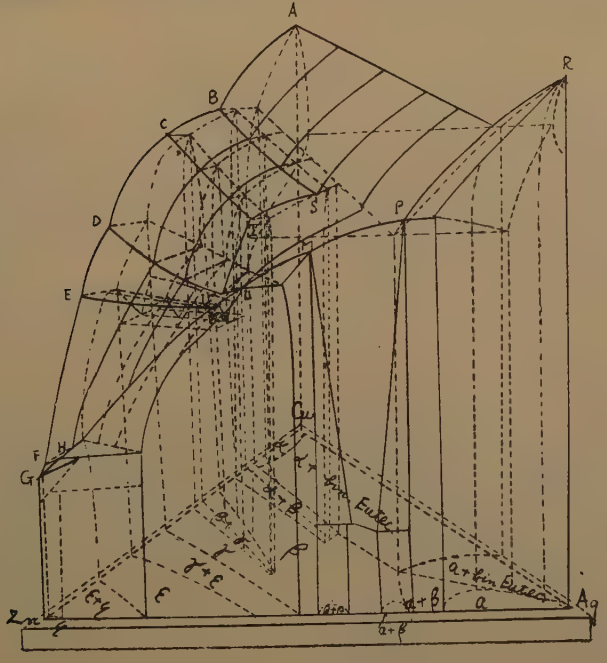
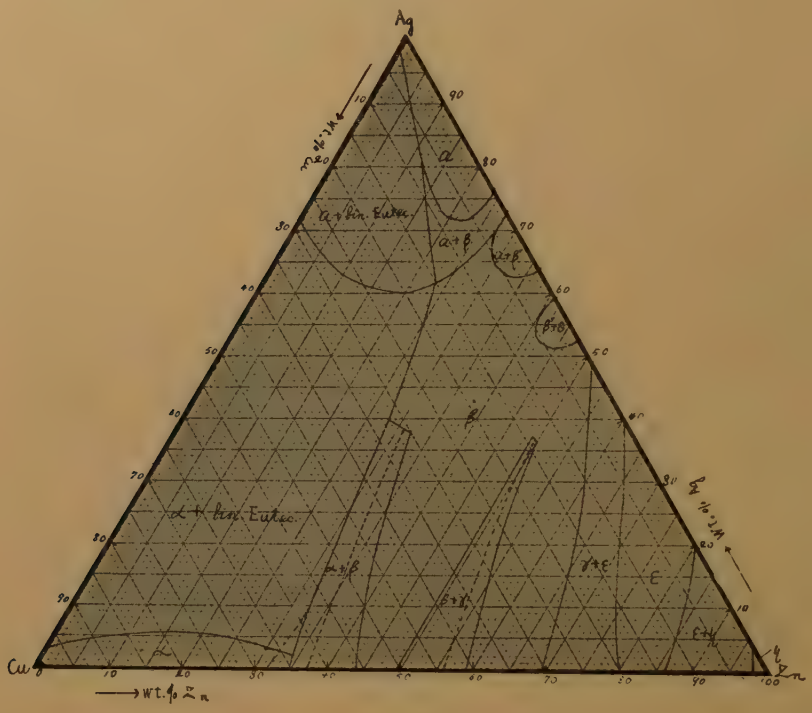

A
B
C
D
E
F
G
H
R
S
P
Cu
Zn
Ag
Eutec
Eutec
Eutec

Fig. 32



In Fig. 32, the full lines refer to the field boundaries at ordinary temperatures, while the dotted lines refer to those at higher temperatures.

In conclusion, the author desires to express his indebtedness to Prof. Dr. M. Chikashige for his kind guidance and valuable advice during the course of the investigation.

Institute for Chemical Research,
Imperial University, Kyoto.

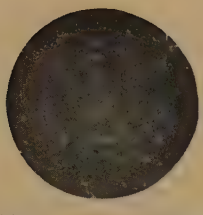


Photo 1. 10%Ag, 10%Zn and 80%Cu. ×150.

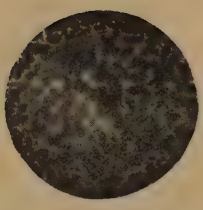


Photo 2. 50%Ag, 10%Zn and 40%Cu ×150.

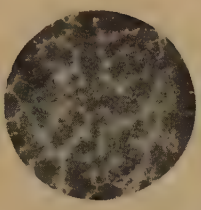


Photo 3. 10%Ag, 17%Zn and 73%Cu. ×150.

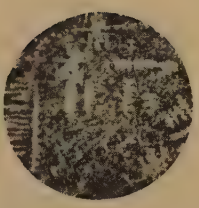


Photo 4. 80%Ag, 10%Zn and 10%Cu. ×150.

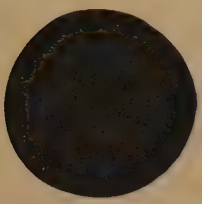


Photo 5. 3%Ag, 10%Zn and 87%Cu. Annealed at 600° for two days. ×150.

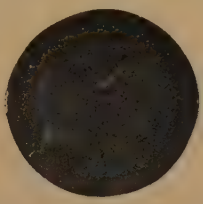


Photo 6. 6%Ag, 10%Zn and 84%Cu. Annealed at 700°. ×150.

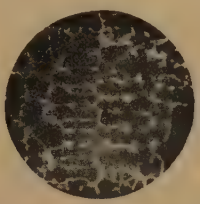


Photo 7. 20%Ag, 20%Zn and 60%Cu. ×150.

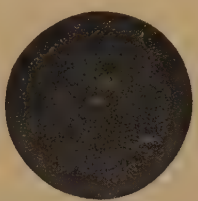


Photo 8. 6%Ag, 20%Zn and 74%Cu. Quenched at 600°. ×150.

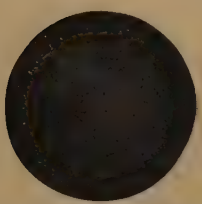


Photo 9. 87%Ag, 10%Zn and 3%Cu. Annealed at 500° for 1 day. ×150.

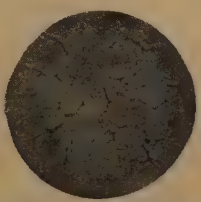


Photo 10. 70%Ag, 20%Zn and 10%Cu. ×150.

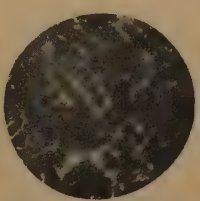


Photo 11. 20%Ag, 30%Zn and 50%Cu. ×150.

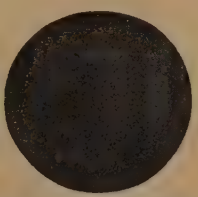


Photo 12. 30%Ag, 40%Zn and 30%Cu. ×150.

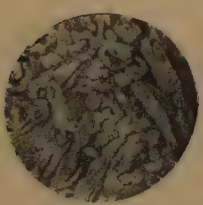


Photo 13. 5%Ag, 40%Zn and 55%Cu. Quenched at 600° after being kept at that temperature for a few minutes. ×150.

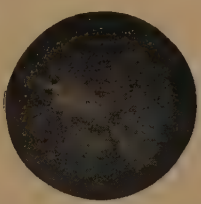


Photo 14. The same alloy quenched at 820° after being kept at that temperature for a few minutes. ×150.

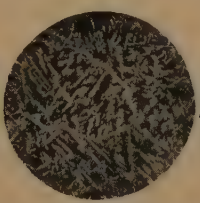


Photo 15. 10%Ag, 40%Zn and 50%Cu. ×150.

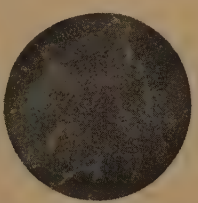


Photo 16. 45%Zn, 2%Cu and 53%Ag. Quenched at 400° after being kept at that temperature for 30° minutes. ×150.

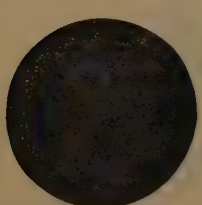


Photo 17. 47%Zn, 3%Cu and 52%Ag. Quenched at 650° after being kept at that temperature for 30 minutes. ×150.

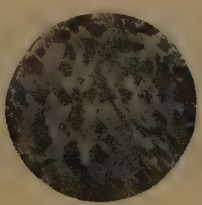


Photo 18. 15%Ag, 33%Zn and 52%Cu. ×150.

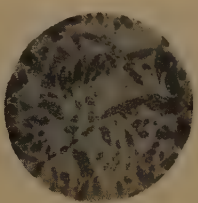


Photo 19. 50%Zn, 20%Ag and 30%Cu. Quenched at 600° after being kept at that temperature for 30 minutes. ×150.

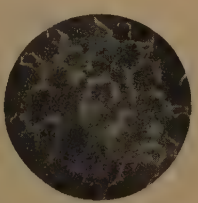


Photo 20. 2%Ag, 55%Zn and 43%Cu. Quenched at 600° after being kept at that temperature for 30 minutes. ×150

Photo 21. The same alloy quenched at 820° after being kept at that temperature for 30 minutes. ×150.

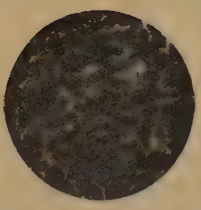


Photo 22. 30%Ag, 50%Zn and 20%Cu. ×150.

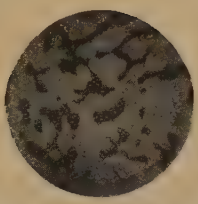


Photo 23. 5%Cu, 55%Zn and 40%Ag. ×150.

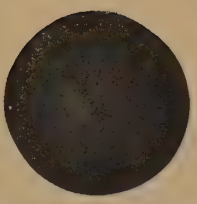


Photo 24. 16%Ag, 65%Zn and 19%Cu. Quenched at 610° after being kept at that temperature for 30 minutes. ×150.

Photo 25. The same alloy quenched at 500° after being kept at that temperature for 30 minutes. ×150.

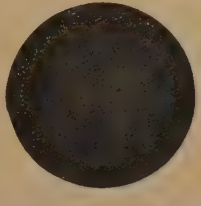


Photo 26. 22%Ag, 65%Zn and 13%Cu. Quenched at that temperature for 30 minutes. ×150.

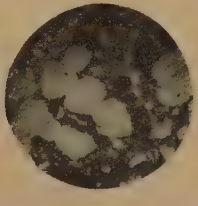


Photo 27. The same alloy quenched at 565° after being kept at that temperature for 30 minutes. ×150.

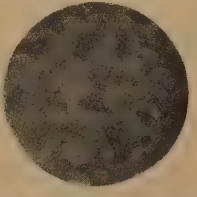


Photo 28. 28%Ag, 65%Zn and 7%Cu. Quenched at 550°. ×150.

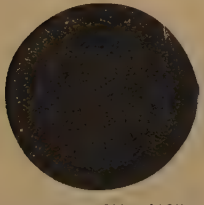


Photo 29. 6%Ag, 70%Zn and 24%Cu. Quenched at 625° after being kept at that temperature for 30 minutes. ×150.

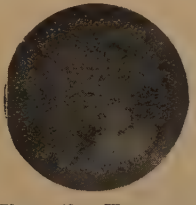


Photo 30. The same alloy quenched at 565° after being kept at that temperature for 30 minutes. ×150.

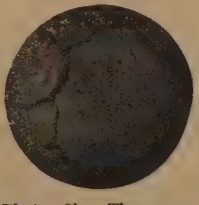


Photo 31. The same alloy quenched at 500° after being kept at that temperature for 30 minutes. ×150.

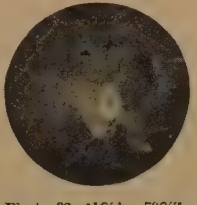


Photo 32. 11%Ag, 70%Zn and 19%Cu. Quenched at 585° after being kept at that temperature for 30 minutes. ×150.

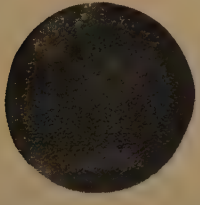


Photo 33. The same alloy quenched at 600° after being kept at that temperature for 30 minutes. ×150.

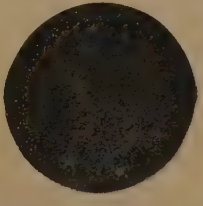


Photo 34. The same alloy quenched at 500° after being kept at that temperature for 30 minutes. ×150.

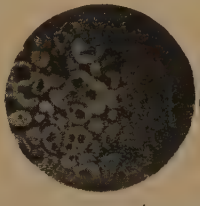
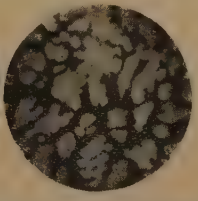


Photo 35. 5%Ag, 84%Zn and 11%Cu. Quenched at 550° ×150.



Bhoto 36. 90%Zn, 5%Ag and 5%Cu. ×150.

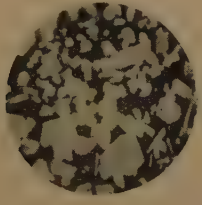


Photo 37. 1%Ag, 4%Cu and 95%Zn. ×150.

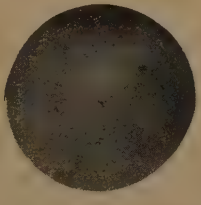
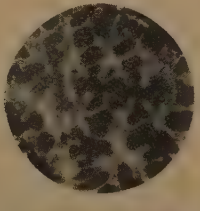


Photo 38. 0.3%Cu, 99%Zn 0.7%Ag. ×150



Bhoto 39. 16%Ag, 65%Zn and 19%Cu. Quenched at 580° after being kept at that temperature for a few minutes.

The Orientation of Single Crystals of Tin

By

Kenzo Tanaka

(Received October 23, 1929)

Abstract

The orientation of many single-crystals of tin, formed by recrystallization in polycrystalline specimens under various conditions, was examined by means of X-rays, to see whether or not it depends upon the previous history of the specimens; and it was found that the dependence of the crystallographic orientation upon the previous treatment was much less than in the case of zinc. The favourable crystallographic direction of growth of the tin crystal was also examined, and it was found to be roughly parallel to the basal plane of the tetragonal crystal.

As a continuation of previous works on aluminium[1] and zinc[2], in which some regularities in the orientation of the crystals depending upon the conditions under which they were formed was found, the same examination was now made with the single-crystals of white tin. The method of determining the orientation of the crystallographic axes by means of X-rays was the same as before, and it was carried out with the aid of the crystallographic globe devised by Prof. U. Yoshida[3]. The orientation of the axes of the test-pieces of single-crystals of tin, was represented in a stereographic projection by taking three crystallographic axes [001], [100] and [110] of the tetragonal crystal of tin as the reference directions.

The material used as the test-pieces was pure commercial tin. Fig. 1 shows the orientation of the crystals formed in test-pieces consisting of plates 0 3 mm. in thickness, which were prepared from cast plate of 3 mms. thickness by rolling, and then by annealing at 200°C for about one day. The crystals formed by this method were

1 Jap. J. Phys., **4**, 137 (1927)
2 These Memoirs, **11**, 361 (1928)
3 Jap. J. Phys., **4**, 133 (1927)

small in size, and only a few of them allowed of examination with X-rays. In Fig. 1 the direction of the surface normal of the plate and that of the rolling are represented by small circles and dots respectively ; and the line joining a small circle and a dot indicates that

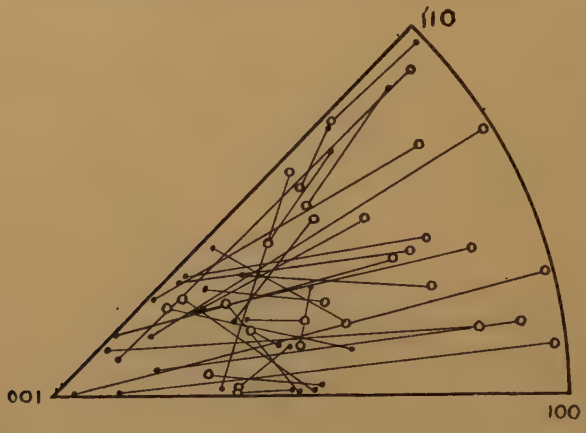


Fig. 1

they belong to same crystal. In this case the scattering of the orientation is very large compared with the corresponding case of the hexagonal crystal of zinc ; and though no definite conclusion can be drawn with regard to the regularity in the crystallographic orientation, we can detect a slight tendency for the normal to the basal plane of the tetragonal crystal of tin to approach the direction of rolling.

Fig. 2 shows the results obtained with the crystals formed in thin

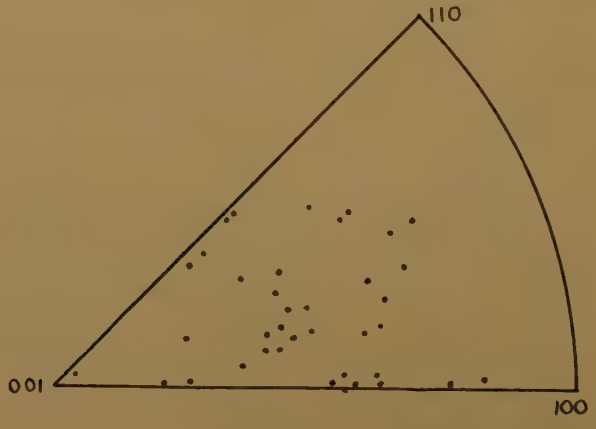


Fig. 2

wires of 1·2 mms. diameter, which were prepared from cast rods of 3 mms. diameter by drawing them through circular dies and then subjecting them to the same heat-treatment as before. In this figure, the distribution of the dots, which represent the direction of the axis of the wire in reference to the crystallographic axes of various tin crystals, shows that it is difficult for a tin crystal to grow in such orientation that the basal plane of it is nearly parallel to the axis of the wire.

Figs. 3 and 4 represent the results of the examination of the crystals

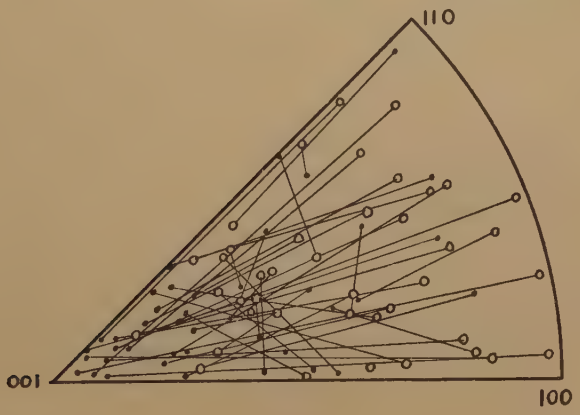


Fig. 3

of tin obtained by the usual stress-annealing method. By this method larger crystals of tin were obtained, as in the case of the other metals. The dimentions of the test-pieces used were the same as before, and

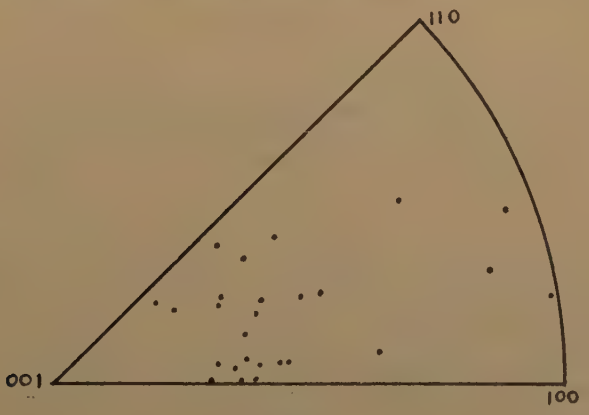


Fig. 4

the stress applied was 1% or 2% extension along the axis of the specimen. In Fig. 3 the small circles and the dots, connected by lines, represent respectively the direction of the surface normal of the plate and that of the stress applied. From this figure, we can see that the dots, the direction of the stress applied, are crowded in the vicinity of the axis [001]. The direction of the stress applied to the wire, that is the axis of the wire, is represented by the dots in Fig. 4. In this case we get a similar result as in the case of aluminium, and the dots are crowded in the vicinity of the [201] axis.

Comparing the results obtained with tin with those of zinc, we can see that the effect of some regular previous treatment of the specimen before recrystallization upon the regularity of the orientation of the crystals is more predominant in zinc than in tin; and in the latter case the scattering of the orientation of the crystals is much greater. This difference in the effect of previous treatment may, at least partially, be attributed to the difference in the recrystallization temperature of these two metals. Tin subjected to cold working recrystallises at room temperature, so that the effect of working will be diminished, at least to some extent, before annealing.

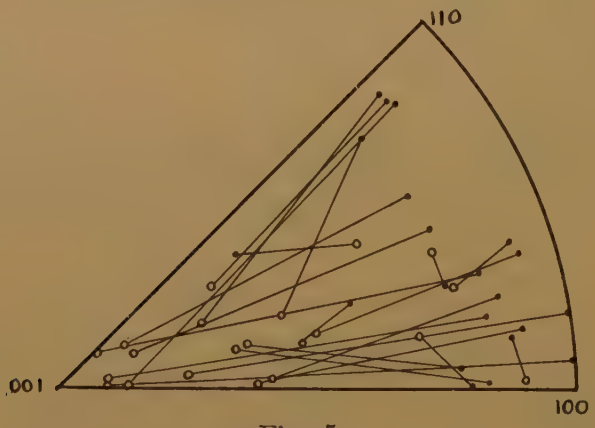


Fig. 5

Next the favourable crystallographic direction of growth of tin was examined. Some tin plates and wires were melted and cooled gradually from one end of the specimen to the other. In Figs. 5 and 6 the dots represent the direction of the advance of the cooling, which may be considered to be the direction of the growth of the crystal formed in the test-pieces of plate and wire respectively; and the small circles in

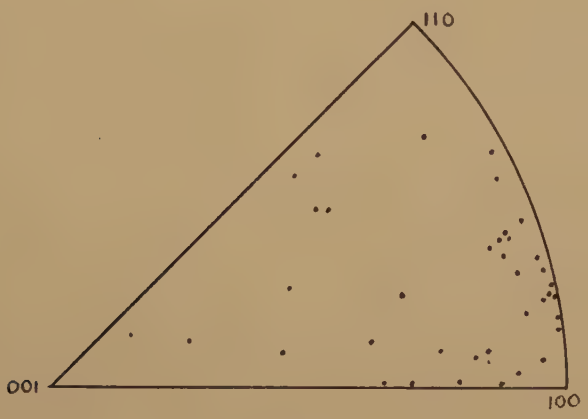


Fig. 6

Fig. 5 indicate the direction of the surface normal of the plate. From these figures, it can be seen roughly that the tin crystal grows somewhat frequently in the direction which is nearly parallel to the basal plane, just as in the case of zinc.

In conclusion, the writer wishes to express his sincere thanks to Prof. U. Yoshida for his kind guidance in the research.

INDEX OF AUTHORS TO VOLUME XII

PAGE

Asagoe, K.—Classification of the Spectral Lines of Cl, Br and I... 275

Fujita, B.—Crystal-Faces developed by etching Metallic Crystals of Aluminium and Zinc 159

Fujiwara, T.—Tensile Strength and Fracture of Rolled Strips of Molybdenum ... 165

Fukami, Y.—The Arrangement of the Micro-Crystals in Compressed Single-Crystal-Plates of Aluminium... 261

Funakoshi, O.—A Sensitive Reaction of Cuprous Ion 155

Ginbayashi, Y. (See **Katagishi, H., Ginbayashi, Y.** and **Matsui, M.**)... 57

Iitsuka, D.—On the Effect of mixing Small Quantities of Cobalt with Brass 179

Ishibashi, M.—Quantitative Analysis of Phosphoric Acid, Part I. Determination as Magnesium Pyrophosphate 23

Ishibashi, M.—Quantitative Analysis of Phosphoric Acid, Part II. New Gravimetric and Volumetric Methods... 39

Ishibashi, M.—Quantitative Analysis of Phosphoric Acid, Part III. Determination as Zinc Ammonium Phosphate 49

Ishibashi, M.—Quantitative Analysis of Phosphoric Acid, Part IV. Gravimetric and Volumetric Determination as Ammonium Phosphomolybdate... 135

Ito, S.—A Simple Method of obtaining a Single-Crystal of Zinc with Approximately any Desired Orientation of its Principal Axis 97

Itomi, H.—The Electrolytic Reduction of O-Nitrobenzene Azophenol 343

Kamimoto, R. (See **Nomitsu, T., Kamimoto, R.** and **Toyohara, Y.**) 265

Katagishi, H., Ginbayashi, Y. and **Matsui, M.**—The Anodic Behabiour of Substituted Acetic Acids, Part I. Diphenylacetic Acid 57

Kotô, H.—On the Reflection of the Ultra-Violet Rays from Metallic Surfaces in Retation to their Micro-Structures 81

Masaki, O.—Studies in Photographic Sensitivity, Part I. The Effect of Heat on the Sensitivity Curve of Photographic Plates 1

Masaki, O.—Studies in Photographic Sensitivity, Part II. On the Sensitivity of Photographic Plates at Various Temperatures 13

Masaki, O.—Studies in Photographic Sensitivity, Part III. Sensitizing Action of Previous Exposure to a Dim Light 107

Masaki, O.—Studies in Photographic Sensitivity, Part IV. Desensitizing Action of Previous Fogging by X-Rays... 117

Masaki, O.—Studies in Photographic Sensitivity, Part V. Effect of Heat on the Absorption Spectrum and Photoelectric Conductivity of Silver Bromide, and their Relation to the Photographic Action 127

Matsui, M. (See **Katagishi, H., Ginbayashi, Y.** and **Matsui, M.**)... 57

PAGE

Matsumiya, K. and **Nakata, H.**—Organic Compounds of Arsinic, VI. Electrolytic Reduction of Some Aryl-Arsinic Acids... 63

Nakata, H. (See **Matsumiya, K.** and **Nakata, H.**) 63

Nomitsu, T., Kamimoto, R. and **Toyohara, Y.**—On the Adsorption of a NaCl-Solution by Sand 265

Ogura, K.—Electrolytic Reduction of Nitriles. Part I 339

Shima, G.—On the Electrolytic Reduction of Aldehydes, Part V. Cinnamic Aldehyde... 69

Shima, G.—On the Electrolytic Reduction of Aldehydes, Part VI. Complete Reduction of the Carbonyl Group 73

Shima, G.—On the Electrolytic Reduction of Ketones, Part I. Reduction of α,β-Unsaturated Ketones... 327

Takeyama, S.—A Method of determining the Direction of the Axis of a Fibrous Arrangement of Micro-Crystals 257

Tanaka, K.—The Orientation of Single-Crystals of Tin 379

Tasaki, M.—Ueber das ternäre System Cu-Sn-Sb 227

Terada, T.—"The Reversal-Like Phenomena" of the Discharge-Figures impressed on Photographic Plates 217

Toyohara, Y. (See **Nomitsu, T., Kamimoto, R.** and **Toyohara, Y.**) 265

Tsuboi, S. (See **Yoshida, U.** and **Tsuboi, S.**) 203

Tsuboi, S.—On the Fibrous Structure in Metals deposited through Difference in Electrolytic Solutional Pressures, Part II 209

Tsuboi, S.—On the Fovourable Direction of Growth of Some Metal-Crystals 223

Tsutsumi, J.—An Examination of the Micro-Crystals of Calcium Carbonate in Molluscan Shells by Means of X-Rays, Part III 199

Ueno, S.—On the Ternary Silver Alloys, I. The System of Silver, Copper and Zinc... 347

Yoshida, U. and **Tsuboi, S.**—Examination of Ice-Crystals by X-Rays... 203

INDEX OF SUBJECTS TO VOLUME XII

PAGE

Absorption Spectrum and Photoelectric Conductivity of Silver Bromide, and their Relation to the Photographic Action. Studies in Photographic Sensitivity, Part V. Effects of Heat on the, (*Masaki*) 127

Acetic Acids, The Anodic Behabiour of Substituted, Part I. Dephenylacetic Acid (*Katagishi, Ginbayashi* and *Matsui*) 57

Adsorption of a NaCl-Solution by Sand, On the, (*Nomitsu, Kamimoto* and *Toyohara*)... 265

Aldehydes, On the Electrolytic Reduction of, Part V. Cinnamic Aldehyde (*Shima*)... 69

Aldehydes, On the Electrolytic Reduction of, Part VI. Complete Reduction of the Carbonyl Group (*Shima*)... 73

Alloys, On the Ternary Silver, I. The System of Silver, Copper and Zinc (*Ueno*) ... 347

Aluminium and Zinc, Crystal-Faces developed by etching Metallic Crystals of, (*Fujita*)... 159

Aluminium, The Arrangement of the Micro-Crystals in Compressed Sinple-Crystal-Plates of, (*Fukami*) 261

Ammonium Phosphomolybdate. Quantitative Analysis of Phosphoric Acid, Part IV. Gravimetric and Volumetric Determination as, (*Ishibashi*) 135

Anodic Behabiour, the, of Substituted Acetic Acids, Part I. Diphenylacetic Acid (*Katagishi, Ginbayashi* and *Matsui*) 57

Arsenic, Organic Compounds of, VI. Electrolytic Reduction of Some Aryl-Arsinic Acids (*Matsumiya* and *Nakata*) 63

Aryl-Arsinic Acids. Organic Compounds of Arsenic, VI. Electrolytic Reduction of Some, (*Matsumiya* and *Nakata*) 63

Axis of a Fibrous Arrangement of Micro-Crystals, A Method of determining the Direction of the, (*Takeyama*) 257

Br and I, Classification of the Spectral Lines of Cl, (*Asagoe*)... 275

Brass, On the Effect of mixing Small Quantities of Cobalt with, (*Iitsuka*) 179

Calcium Carbonate in Molluscan Shells by Means of X-Rays, Part III. An Examination of the Micro-Crystals of, (*Tsutsumi*) 199

Carbonyl Group. On the Electrolytic Reduction of Aldehydes, Part VI. Complete Reduction of the, (*Shima*) 73

Cinnamic Aldehyde. On the Electrolytic Reduction of Aldehydes, Part V., (*Shima*) ... 69

Cl, Br and I, Classification of the Spectral Lines of, (*Asagoe*)... 275

Cobalt with Brass, On the Effect of mixing Small Quantities of, (*Iitsuka*) 179

Compressed Single-Crystal-Plates of Aluminium, The Arrangement of the Micro-Crystals in, (*Fukami*) 261

Copper and Zinc, On the Ternary Silver Alloys, I. The System of Silver, (*Ueno*) ... 347

Crystal of Zinc with Approximately any Desired Orientation of its Principal Axis. A Simple Method of obtaining a Single-, (*Ito*) 97

Crystal-Faces developed by etching Metallic Crystals of Aluminium and Zinc (*Fujita*) ... 159

Crystals of Aluminium and Zinc, Crystal-Faces developed by etching Metallic, (*Fujita*) .. 159

PAGE

Crystals by X-Rays, Examination of Ice-, (*Yoshida* and *Tsuboi*) 203
Crystals, On the Favourable Direction of Growth of Some Metal-(*Tsuboi*) 223
Crystal-Plates of Aluminium, The Arrangement of the Micro-Crystals in Compressed Single-, (*Fukami*) 261
Crystals of Tin, The Orientation of Single-, (*Tanaka*)... 375
Cu-Sn-Sb, Ueber das ternäre System, (*Tasaki*) 227
Cuprous Ion, A Sensitive Reaction of, (*Funakoshi*) 155
Desensitizing Action of Previous Fogging by X-Rays. Studies in Photographic Sensitivity, Part IV., (*Masaki*) 117
Dim Light, Studies in Photographic Sensitivity, Part III. Sensitizing Action of Previous Exposure to a, (*Masaki*) 107
Diphenylacetic Acid. The Anodic Behabiour of Substituted Acetic Acids, Part I., (*Katagishi*, *Ginbayashi* and *Matsui*) 57
Discharge-Figures impressed on Photographic Plates, "The Reversal-Like Phenomena" of the, (*Terada*)... 217
Electrolytic Reduction of Some Aryl-Arsinic Acids. Organic Compounds of Arsenic VI., (*Matsumiya* and *Nakata*)... 63
Electrolytic Reduction of Aldehydes, On the, Part V. Cinnamic Aldehyde (*Shima*) ... 69
Electrolytic Reduction of Aldehydes, On the, Part VI. Complete Reduction of the Carbonyl Group (*Shima*) 73
Electrolytic Reduction of Ketones, On the, Part I. Reduction of α,β-Unsaturated Ketones (*Shima*) 327
Electrolytic Reduction of Nitriles, Part I (*Oguma*) 339
Electrolytic Reduction of O-Nitrobenzene Azophenol, The, (*Itomi*) 343
Electrolytic Solutional Pressures, Part II. On the Fibrous Structure in Metals deposited through Difference in, (*Tsuboi*) 209
Fibrous Arrangement of Micro-Crystals, A Method of determing the Direction of the Axis of a, (*Tukeyama*) 257
Fibrous Structure in Metals deposited through Difference in Electrolytic Solutional Pressures, Part II. On the, (*Tsuboi*) 209
Fracture of Rolled Strips of Molybdenum, Tensile Strength and, (*Fujiwara*) 165
Gravimetric and Volumetric Methods, Quantitative Analysis of Phosphoric Acid, Part II. New, (*Ishibashi*) 39
Gravimetric and Volumetric Determination as Ammonium Phosphomolybdate. Quantitative Analysis of Phosphoric Acid, Part IV., (*Ishibashi*)... 135
Growth of Some Metal-Crystals, On the Favourable Direction of, (*Tsuboi*) 223
Heat, Studies in Photographic Sensitivity, Part I. The Effect of, on the Sensitivity Curve of Photographic Plates (*Masaki*) 1
Heat on the Absorption Spectrum and Photoelectric Conductivity of Silver Bromide, and their Relation to the Photographic Action. Studies in Photographic Sensitivity, Part V. Effects of (*Masaki*)... 127
I, Classification of the Spectral Lines of Cl, Br and, (*Asagoe*) 275
Ice-Crystals by X-Rays, Examination of, (*Yoshida* and *Tsuboi*)... 203
Ion, A Sensitive Reaction of Cuprous, (*Funakoshi*) 155
Ketones, On the Electrolytic Reduction of, Part I. Reduction of α,β–Unsaturated Ketones (*Shima*) 372
Magnesium Pyrophosphate, Quantitative Analysis of Phosphoric Acid, Part I. Determination as, (*Ishibashi*) 23

PAGE
Metal-Crystals, On the Favourable Direction of Growth of Some, (*Tsuboi*) 223
Metallic Crystals of Aluminium and Zinc, Crystal-Faces developed by etching, (*Fujita*)... 159
Metallic Surfaces in Relation to their Micro-Structures. On the Reflection of the Ultra-Violet Rays from, (*Kotô*)... 81
Metals deposited through Difference in Electrolytic Solutional Pressures, Part II. On the Fibrous Structure in, (*Tsuboi*)... 209
Micro-Crystals of Calcium Carbonate in Molluscan Shells by Means of X-Rays, Part III. An Examination of the, (*Tsutsumi*) 199
Micro-Crystals, A Method of determining the Direction of the Axis of a Fibrous Arrangement of, (*Takeyama*) 257
Micro-Crystals in Compressed Single-Crystal-Plates of Aluminium, The Arrangement of the, (*Fukami*) 261
Micro-Structures. On the Reflection of the Ultra-Violet Rays from Metallic Surfaces in Relation to their, (*Kotô*) 81
Molluscan Shells by Means of X-Rays, Part III. An Examination of the Micro-Crystals of Calcium Carbonate in, (*Tsutsumi*) 199
Molybdenum, Tensile Strength and Fracture of Rolled Strips of, (*Fujiwara*) 165
NaCl-Solution by Sand, On the Adsorption of a, (*Nomitsu, Kamimoto* and *Toyohara*)... 265
Nitriles, Electrolytic Reduction of, Part I (*Ogura*) 339
Nitrobenzene Azophenol, The Electrolytic Reduction of O-, (*Itomi*) 343
Organic Compounds of Arsenic, VI. Electrolytic Reduction of Some Aryl-Arsinic Acids (*Matsumiya* and *Nakata*) 63
Phosphoric Acid, Quantitative Analysis of, Part I. Determination as Magnesium Pyrophosphate (*Ishibashi*)... 23
Phosphoric Acid, Quantitative Analysis of, Part II. New Gravimetric and Volumetric Methods (*Ishibashi*) 39
Phosphoric Acid, Quantitative Analysis of, Part III. Determination as Zinc Ammonium Phosphate (*Ishibashi*) 49
Phosphoric Acid, Quantitative Analysis of, Part IV. Gravimetric and Volumetric Determination as Ammonium Phosphomolybdate (*Ishibashi*) 135
Photoelectric Conductivity of Silver Bromide, and their Relation to the Photographic Action. Studies in Photographic Sensitivity, Part V. Effects of Heat on the Absorption Spectrum and, (*Masaki*) 127
Photographic Action. Studies in Photographic Sensitivity, Part V. Effects of Heat on the Absorption Spectrum and Photoelectric Conductivity of Silver Bromide, and their Relation to the, (*Masaki*) 127
Photographic Plates, Studies in Photographic Sensitivity, Part I. The Effect of Heat on the Sensitivity Curve of (*Masaki*) 1
Photographic Plates at Various Temperatures, Studies in Photographic Sensitivity, Part II. On the Sensitivity of, (*Masaki*) 13
Photographic Plates, "The Reversal-Like Phenomena" of the Discharge-Figures impressed on, (*Terada*) 217
Photographic Sensitivity, Studies in, Part I. The Effect of Heat on the Sensitivity Curve of Photographic Plates (*Masaki*)... 1
Photographic Sensitivity, Studies in, Part II. On the Sensitivity of Photographic Plates at Various Temperatures (*Masaki*)... 13
Photographic Sensitivity, Studies in, Part III. Sensitizing Action of Previous Exposure to a Dim Light (*Masaki*) 107

PAGE

Photographic Sensitivity, Sftudies in, Part IV. Desensitizing Action of Previous Fogging by X-Rays (*Masaki*)... 117

Photographic Sensitivity, Studies in, Part V. Effects of Heat on the Absorption Spectrum and Photoelectric Conductivity of Silver Bromide, and their Relation to the Photographic Action (*Masaki*) 127

Previous Fxpesure to a Dim Light. Studies in Photographic Sensitivity, Part III. Sensitizing Action of, (*Masaki*) 107

Previous Fogging by X-Rays. Studies in Photographic Sensitivity, Part IV. Desensitizing Action of, (*Masaki*) 117

Principal Axis. A Simple Method of obtaining a Single-Crystal of Zinc with Approximately any Desired Orientation of its, (*Ito*) 97

Quantitative Analysis of Phosphoric Acid, Part I. Determination as Magnesigm Pyrophosphate (*Ishibashi*) 23

Quantitative Analysis of Phosphoric Acid, Part II. New Gravimetric and Volumetric Methods (*Ishibashi*) 39

Quantitave Analysis of Phosphoric Acid, Part III. Determination as Zinc Ammonium Phosphate (*Ishibashi*) 49

Quantitative Analysis of Phosphoric Acid, Part IV. Gravimetric and Volumetric Determination as Ammonium Phosphomolybdate (*Ishibashi*) 135

Reaction of Cuprous Ion, A Sensitive, (*Funakoshi*) 155

Reduction of the Carbonyl Group. On the Electrolytic Reduction of Aldehyde, Part VI. Complete, (*Shima*) 73

Reduction of α,β-Unsaturated Ketones. On the Electrolytic Reduction of Ketones, Part I., (*Shima*)... 327

Reduction of Nitriles, Electrolytic, Part I (*Ogura*) 339

Reduction, The Electrolytic, of o-Nitrobenzene Azophenol, (*Itomi*)... 343

Reflection of the Ultra-Violet Rays from Metallic Surfaces in Relation to their Micro-Structures. On the, (*Kotô*) 81

Reversal-Like Phenomena" of the Discharge-Figures impressed on Photographic Plates. "The, (*Terada*) 217

Rolled Strips of Molybdenum, Tensile Strength and Fracture of, (*Fujiwara*) 265

Sand, On the Adsorption of a NaCl-Solution by, (*Nomitsu*, *Kamimoto* and *Toyohara*)... 265

Sb, Ueber das ternäre System Cu-Sn-, (*Tasaki*) 227

Sensitivity Curve of Photographic Plates, Studies in Photographic Sensitivity, Part I. The Effect of Heat on the, (*Masaki*) 1

Sensitivity of Photographic Plates at Various Temperatures, Studies in Photographic Sensitivity, Part II. On the, (*Masaki*)... 13

Sensitizing Action of Previous Exposure to a Dim Light. Studies in Photographic Sensitivity, Part III., (*Masaki*) 107

Silver, Copper and Zinc, On the Ternary Silver Alloys, I. The System of, (*Ueno*) ... 347

Silver Bromide, and their Relation to the Photographic Action. Studies in Photographic Sensitivity, Part V. Effects of Heat on the Absorption Spectrum and Photoelectric Conductivity of, (*Masaki*)... 127

Single-Crystal of Zinc with Approximately and Desired Orientation of its Principal Axis. A Simple Method of obtaining a, (*Ito*) 97

Single-Crystal-Plates of Aluminium, The Arrangement of the Micro-Crystals in Compressed, (*Fukami*) 261

Single-Crystals of Tin, The Orientation of, (*Tanaka*) 375

PAGE
Sn-Sb, Ueber das ternäre System Cu-, (*Tasaki*) 227
Solutional Pressures, Part II. On the Fibrous Structure in Metals deposited through Difference in Electrolytic, (*Tsuboi*) 209
Spectral Lines of Cl, Br and I, Classification of the, (*Asagoe*)... 275
Tensile Strength and Fracture of Rolled Strips of Molybdenum (*Fujiwara*) 165
Ternäre System Cu-Sn-Sb, Ueber das, (*Tasaki*) 227
Ternary Silver Alloys, On the, I. The System of Silver, Copper and Zinc (*Ueno*) ... 347
Tin, The Orientation of Single-Crystals of, (*Tanaka*) 375
Ultra-Violet Rays from Metallic Surfaces in Relation to their Micro-Structures. On the Reflection of the, (*Kotô*)... 81
Volumetric Methods. Quantitative Analysis of Phosphoric Acid, Part II. New Gravimetric and, (*Ishibashi*) 39
Volumetric Determination as Ammonium Phosphomolybdate. Quantitative Analysis of Phosphoric Acid, Part IV. Gravimetric and, (*Ishibashi*)... 135
X-Rays. Studies in Photographic Sensitivity, Part IV. Desensitizing Action of Previous Fogging by, (*Masaki*) 117
X-Rays, Part III. An Examination of the Micro-Crystals of Calcium Carbonate in Molluscan Shells by Means of, (*Tsutsumi*) 199
X-Rays, Examination of Ice-Crystals by, (*Yoshida* and *Tsuboi*)... 203
Zinc Ammonium Phosphate. Quantitative Analysis of Phosphoric Acid, Part III. Determination as, (*Ishibashi*) 49
Zinc with Approximately any Desired Orientation of its Principal Axis. A Simple Method of obtaining a Single-Crystal of, (*Ito*) 97
Zinc, Crystal-Faces developed by etching Metallic Crystals of Aluminium and, (*Fujita*)... 159
Zinc, On the Ternary Silver Alloys, I. The System of Silver, Copper and, (*Ueno*) 347

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CONTENTS

Classification of the Spectral Lines of Cl, Br and I
By Kwan-ichi Asagoe 275
On the Electrolytic Reduction of Ketones. Part I: Reduction of α,β-Unsaturated Ketones
By Goro Shima 327
Electrolytic Reduction of Nitriles. Part I
By Kōichiro Ogura 339
The Electrolytic Reduction of o-Nitrobenzene Azophenol
By Hidemaru Itomi 343
On the Ternary Silver Alloys. I: The System of Silver, Copper and Zinc
By Shûzô Ueno 347
The Orientation of Single Crystals of Tin
By Kenzo Tanaka 375